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SIMULTANEOUS CHEMICAL REACTION AND
DISTILLATION OF FORMALDEHYDE

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Doctor of Philosophy
by
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DISTILLATION OF FORMALDEHYDE

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SUMMARY

The thesis is concerned with the development and testing of a mathematical model of a distillation process in which the components react chemically.

The formaldehyde-methanol-water system was selected and only the reversible reactions between formaldehyde and water giving methylene glycol and between formaldehyde and methanol producing hemiformal were assumed to occur under the distillation conditions. Accordingly the system has been treated as a five component system.

The vapour-liquid equilibrium calculations were performed by solving iteratively the thermodynamic relationships expressing the phase equilibria with the stoichiometric equations expressing the chemical equilibria. Using optimisation techniques, the Wilson single parameters and Henry's constants were calculated for binary systems containing formaldehyde which was assumed to be a super-critical component whilst Wilson binary parameters were calculated for the remaining binary systems. Thus the phase equilibria for the formaldehyde system could be calculated using these parameters and good accuracy was obtained when calculated values were compared with experimental values.

The distillation process was modelled using the mass and energy balance equations together with the phase equilibria calculations. The plate efficiencies were obtained from a modified A.I.Ch.E. Bubble Tray method. The resulting equations were solved by an iterative plate to plate calculation based on the Newton Raphson method.

Experiments were carried out in a 76mm I.D., eight sieve plate distillation column and the results were compared with the mathematical model calculations. Overall, good agreement was obtained but some discrepancies were observed in the concentration profiles and these may have been caused by the effect of limited physical property data and a limited understanding of the reactions mechanism.

The model equations were solved in the form of modular computer programs. Although they were written to describe the steady state distillation with simultaneous chemical reaction of the formaldehyde system, the approach used may be of wider application.

SIMULATION DISTILLATION CHEMICAL REACTION FORMALIN

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LIST OF PRINCIPAL SYMBOLS

A, B, C	Constants of equations for efficiency correction
a, b, c	Constants of equation defining liquid molar volume in terms of temperature
B, C, D	Constants of virial equation
Chl-3	Constants of equation defining heat capacities in terms of temperature
Cp	Heat capacity
DE	Eddy diffusivity
DG	Gas diffusivity
DHV	Heat of vaporisation
DL	Liquid diffusivity
E	Plate efficiency
EO	Point efficiency
F	Feed molar flow rate
F ₀ -F ₃	Functions for calculation of second virial coefficients
FF	F factor in plate efficiency calculations
f	Fugacity
fr	Local mole fraction in liquid
G	Free energy
H	Henry's constant
H _n	Enthalpy at stage n
HR	Heat of reaction
hl-5	Enthalpy of pure component

hf	Froth height
hL	Height of clear liquid on a plate
hrl-2	Molar heat of reactions
K	Chemical reaction equilibrium constant
k	Chemical reaction rate constant
L	Liquid molar flow rate (before reactor)
LF	Liquid rate per width of plate
LM	Pure liquid molar volume
Lmix	Liquid molar volume (mixture)
LR	Liquid molar flow rate (after reactor)
ℓ	Liquid travel across the plate
M	Total number of data sets
m	Number of components
N	Total number of distillation stages
NF	Feed plate location
NG	Gas phase transfer unit
NL	Liquid phase transfer unit
NOG	Overall transfer unit
n	Number of moles
Pe	Peclet number
p	Partial pressure
Q	Heat input
R	Total reacted number of moles
r	Reacted number of moles for specific component
S	Cross sectional area
Sc	Schmidt number

SL	Slope of equilibrium curve
T	Temperature
T_b	Normal boiling temperature
tL	Liquid residence time on the plate
U	Partial molar property
UG	Vapour rate
V	Molar volume
V_n	Vapour molar flow rate (before reactor) on stage n
Vmix	Molar volume of mixture
VR	Vapour molar flow rate (after reactor)
v	Liquid partial molar volume
w	Average width of plate
wh	Weir height
X	Liquid mole fraction
X_n	Liquid mole fraction (before reactor) on stage n
XF	Feed mole fraction
X01-5	Original liquid mole fraction
XR	Liquid mole fraction (after reactor)
Y	Vapour mole fraction
Y_n	Vapour mole fraction (before reactor) on stage n
Y01-5	Original vapour mole fraction
YR	Vapour mole fraction (after reactor)
Z	Compressibility factor

Gas phase

Greek Letters

α	Number of moles, consumed in the reaction of formaldehyde with water
β	Number of moles, consumed in the reaction of formaldehyde with methanol
γ	Activity coefficient
ΔE_{1-2}	Difference of actual and calculated efficiencies of sections below or above feed plate
ΔH	Enthalpy difference
ϵ	Viscosity
η	Association factor
Λ	Wilson parameter
λ	Wilson energy parameter
μ	Chemical potential
μd	Dipole moment
μ_r	Reduced dipole moment
π	Potential energy parameter
ρ	Density
ϕ	Fugacity coefficient
ω	Acentric factor
ω_H	Acentric factor of homomorph of the component

Subscripts

b	Reboiler stage
c	Critical
G	Gas phase

i, j, k	Component
L	Liquid phase
Lmix	Liquid mixture
m	Mixture
mv	Murphree efficiency, defined for the vapour
n	Stage number
r	Reference
T	Total number
V	Vapour phase
Vmix	Vapour mixture
1,2	Component or reaction number

Superscripts

F	Feed
L	Liquid
^r P	Reference pressure
s	Saturation
V	Vapour
o	Standard state
i	Constants of volume explicit virial equation
∞	Infinite dilution
*	Equilibrium

LIST OF SYMBOLS FOR COMPUTER PROGRAMS

AA-DD	Constants of equations for enthalpy
ALF,ALFA	α
BET,BETA	β
BFT	Reboiler efficiency
CACTCO	Parameters for activity coefficients
CHENRY	Constants for temperature dependence of Henry's constant
CK1-2	Chemical equilibrium constants
CODE	Code number of the experiments
COMPI	Constants of equation for efficiency correlation
CPSAT	Constants for vapour pressure equation
CVLIQ	Constants for liquid molar volume
CVLIQL	Constants for partial molar volume at infinite dilution
DATA	Data matrix
DHV	Heat of vaporisation
DIEF	Difference of actual and calculated efficiencies
DIFL	Liquid diffusivity
DIFV	Vapour diffusivity
DIPOLE	Dipole moment
DRL1-2	Molar heat of reaction 1 and 2
EFF	Plate efficiency
ELL	Liquid rate per width of plate
ENTF	Enthalpy of the feed
ENTLR	Enthalpy of the liquid

ENTVR	Enthalpy of the vapour
ERR	Permitted error of distillation calculation
E2	Permitted error in Newton-Raphson calculation
F	Fugacity
FFCT	F factor
FFD	Feed molar flow rate
FLIQR	Liquid molar flow rate
FLPRO	Top product molar flow rate
FREFER	Reference state fugacity
FVAPR	Vapour molar flow rate
GAMMA	Activity coefficient
GRAD	Gradient of equilibrium curve
HENRY	Henry's constant
HF	Froth height
HL	Liquid height
HT	Enthalpy of the mixture
HTP	Enthalpy of the component
IC	Number of constants in equation for correction of efficiency
IP	Number of section in distillation column for efficiency correction
IPRINT	Printing interval
ITRAY	Feed tray
KL1-2	Liquid chemical equilibrium constants
NCOMP	Number of components
NCRIT	Number of supercritical components
NEF	Component number whose efficiency is calculated by difference.

NPARAM	Number of parameters
NPTS	Number of points
NREFER	Reference component's number
NTRAY	Number of trays
OMEGA	Acentric factor
OMEGAH	Acentric factor of homomorph of polar component
P	Pressure
PARAM	Parameter matrix
PCAL	Calculated pressure
PCRIT	Critical pressure
PEFF	Point efficiency
PHI	Vapour phase fugacity coefficient
PSAT	Vapour pressure
Q	Heat input
RG	Vapour density
RRATIO	Reflux ratio
S	Difference of sum of temperatures in successive iterations
T	Temperature
TB	Normal boiling temperature
TCRIT	Critical temperature
TF	Feed temperature
TL	Residence time
TPRT	Temperature of top product
TREF	Reference temperature
TUNL	Liquid phase transfer unit

TUNV	Vapour phase transfer unit
UG	Vapour rate
V	Weir height
VCRIT	Critical volume
VIS	Liquid component viscosity
VISCL	Liquid mixture viscosity
VISCV	Vapour mixture viscosity
VLIQ	Liquid molar volume
VLIQL	Partial molar volume at infinite dilution
VO	Liquid molar volume at infinite dilution
WM	Molecular weight
X,XR	Liquid mole fraction
XDM1-3	Mole fractions of original liquid
XRF	Feed mole fraction
Y,YR	Vapour mole fraction
YDM1-3	Mole fraction of original vapour
Z1-4	Liquid mole fraction

CHAPTER 1

INTRODUCTION

1. INTRODUCTION

1.1 DISTILLATION

The important separation technique of distillation is widely used in industry. In distillation the components of a mixture are distributed between the vapour and liquid phases. In other separation processes a separating agent is usually introduced into the mixture in order to provide a second phase, as for example, in gas absorption and solvent extraction, whilst in distillation the new phase is created from the original solution utilising heat as the separating agent.

Distillation can be carried out when all the components of a system are volatile and have different vapour pressures for different components at one temperature. The components under distillation are subjected to repeated vaporisation and condensation, where the more volatile components are transferred to the vapour phase.

However, some limitations are involved in the selection of distillation as a separation process. In absorption or solvent extraction where a separating agent is selected for the removal process, a choice of the most adequate separating agent can be made from a wide variety of solvents. But in distillation, the vapour which will be created from the liquid, eventually will be composed of the components present in the liquid phase. Therefore the vapour would

be chemically very similar to the liquid and the change in the composition resulting from the distribution of the components between the two phases may not be very large.

Nevertheless, distillation has become one of the most important mass transfer operations because direct separation by distillation into relatively pure components, requiring no further processing can be achieved.

In all mass transfer operations, components are transferred by diffusion in at least one or often in both phases. In distillation the most volatile component is transferred through the liquid phase to the interface by diffusion and away from the interface into the vapour. The least volatile component is removed in the reverse direction through the vapour into the liquid. Thus the separation of molecules in distillation is caused by the process of diffusion.

1.2 DISTILLATION WITH CHEMICAL REACTION

The employment of multistage distillation in which reversible chemical reactions take place is becoming more common in chemical industries. Esterification, transesterification and acetylation reactions, for example, can be carried out in a distillation column.

Such a type of operation can be particularly suitable if one of the reaction products is the most volatile

component in the mixture. A further advantage is gained as the concentration of the most volatile reaction product will be reduced in the liquid phase and thus the rate of reaction will be enhanced.

Similar arguments can be applied to systems where strongly associating components are being distilled. In these cases, the character of the components under distillation is changed by the effect of the chemical reaction which introduces new associated forms of the components. The complexity of the system is increased by the effect of the chemical reaction as the associated form of the components only exists in the mixture of the solution and thus the isolation of these associated components in the pure form is very difficult. Sophisticated analytical techniques are required for the investigation of such systems in order to determine the reaction mechanisms in a mixture and often the results are considered to be in doubt.

The knowledge of accurate vapour-liquid equilibrium data is one of the essential requirements for the design of a distillation column and its related equipment. Equilibrium between the phases is used as part of the basis for most of the operations involved in chemical engineering. A condition of equilibrium between two or more phases is implied by the use of the term phase equilibria.

Techniques for calculating vapour-liquid equilibrium for multicomponent mixtures must be considered because of the numerous vapour and liquid mixtures which occur in technological processes. Thermodynamic relationships can be used to define the phase equilibria. The desired calculation technique can be obtained from the solution of these thermodynamic relationships.

The equations describing the phase and chemical equilibria must be satisfied simultaneously for both phases. The equations defining the phase and chemical equilibria are defined by thermodynamic relationships. Then the thermodynamic equations for the chemical equilibria are combined with the thermodynamic relationships defining the phase equilibria to give the working equations for the calculations. Secondly, the chemical equilibria can be expressed by stoichiometric equations which are solved simultaneously with the thermodynamic relationships for the phase equilibria..

Distillation calculations for systems with chemical reaction can be solved similarly to the conventional systems with no chemical reaction, except that the chemical reaction must be included in the equations defining the mass and energy balance of each tray in the distillation column.

1.3 DISTILLATION OF FORMALDEHYDE SOLUTIONS

The selection of a system for the investigations was influenced by the interest from the industries involved in the manufacture of formaldehyde. In most of the formaldehyde production methods a solution of formaldehyde in methanol and water is obtained. Distillation is then used for the separation of the components. However, the unusual behaviour of the formaldehyde in the polar solvents reduces the accuracy of the conventional design procedures in distillation. Therefore an understanding of the problems in the distillation of formaldehyde is most welcome by the designers in this area.

When the phase equilibria and distillation calculations are applied to the formaldehyde system, information on the reactions occurring in the system must be available. The most significant reactions in the system of formaldehyde-methanol-water are assumed to be the equilibrium between formaldehyde-water producing methylene glycol and between formaldehyde-methanol producing hemiformal. The reactions leading to the heavy polymers are assumed to be insignificant in the distillation because of the high temperatures and the requisite long reaction time. The production of the polymers is discouraged by high temperatures and some reactions require a

few days to complete. Apart from the polymers, the reaction products have been found to be highly unstable and to exist only in chemical equilibrium in solution. Methylene glycol and hemiformal have not yet been isolated in the pure form and thus the evaluation of the pure component property data needed in the distillation calculations cannot be experimentally determined. Even the critical properties of formaldehyde cannot be measured experimentally, due to decomposition of formaldehyde at high temperatures and pressures. The lack of reliable design procedures for operations involving formaldehyde in polar solvents has been caused by the combination of the complex chemistry of the reactions of formaldehyde together with the instability of the reaction products.

Due to the chemical reactions which occur in both vapour and liquid phases, a solution of formaldehyde-water is comprised of a ternary mixture of formaldehyde-methylene glycol-water and a solution of formaldehyde-methanol-water is comprised of a quinary mixture of formaldehyde-hemiformal-methanol-methylene glycol-water.

1.4 SUMMARY OF ACHIEVEMENTS

Several chemical engineering subjects, such as vapour-liquid equilibrium, reaction kinetics, distillation and stage efficiency, have been combined to model the distillation of formaldehyde solutions. In this initial attempt to model the formaldehyde system, inadequate data

was frequently encountered and some uncertainty over the chemical reactions of formaldehyde with water and methanol was observed. Thus these problems had to be overcome either by using the existing data or by estimation techniques.

The thermodynamic relationships expressing the phase equilibria including the effect of chemical reactions in the liquid and vapour phases, were applied to the ternary and quinary systems. Thus a model was obtained based on the theory of the phase equilibria of the reacting systems (Chapter 3).

The tray to tray method of calculation for the distillation column was found to provide convergent results for the system. This model combined with the model developed for the phase equilibria, was applied in the form of computer programs (Chapters 4 and 5).

The calculated results were compared with experimental data obtained from an 8 sieve plate 76 mm diameter glass distillation column (Chapter 7). The distillation column was designed to allow a number of parameters to be varied from one experiment to another (Chapter 6). Thus the performance of the mathematical model was obtained from the comparison of the results in the various experiments.

Good agreement was achieved for both the phase equilibria and the distillation models. The results from various programs and experiments can be found in the Appendix section.

1. SOLUTIONS

1.1. FORMALDEHYDE

Formaldehyde is one of the group of chemical

compounds which are known as Lichig's (1)

or aliphatic

compounds and

is known as 60.

Formaldehyde (2). The

formaldehyde is a very difficult

to handle and more difficult.

Formaldehyde is prepared from

CHAPTER 2

FORMALDEHYDE SOLUTIONS

Formaldehyde was later to become

Formaldehyde

Formaldehyde

Formaldehyde

Formaldehyde

Formaldehyde

Formaldehyde

Formaldehyde

Formaldehyde

Formaldehyde

Formaldehyde

Formaldehyde

Formaldehyde

Formaldehyde

2. FORMALDEHYDE SOLUTIONS

2.1 DISCOVERY OF FORMALDEHYDE

One of the first reports on the group of chemical compounds known as aldehydes was found in Liebig's (1) research on acetaldehyde in 1835. Other aliphatic aldehydes such as propionaldehyde, butyraldehyde and isovaleraldehyde were then discovered before 1860. Formaldehyde was discovered in 1859 by Butlerov (2). The delay was caused by the chemical instability of formaldehyde which made the isolation of this compound more difficult.

In 1868 A.W. Hofmann (3) prepared formaldehyde by oxidising methanol vapour with air over a heated platinum spiral, and formaldehyde was positively identified as the product. This method was later to become one of the main production techniques.

2.2 FORMALDEHYDE PRODUCTION

Different production methods were developed depending on the availability of raw materials and the required state of the formaldehyde product. Because of its simplicity, the reduction of carbon dioxide has been the subject of considerable study (4-6). Formaldehyde is generally produced from the oxidation of methanol by passing a mixture of air and methanol over a heated catalyst. The product gas is scrubbed with water to dissolve the formaldehyde. Various investigations concerning the reaction in the gas or the liquid phase have been carried out (5, 7-26). The

oxidation of hydrocarbon gases has been used as an alternative method for the production of formaldehyde. Formaldehyde and other chemical compounds are formed in the reaction products. The ratio of the different reaction products is affected by the hydrocarbon raw materials and the reaction techniques employed (27-33, 37-40).

The different techniques of production of formaldehyde are covered by numerous patents and these have been summarised by Walker (41).

2.3 REACTIONS OF FORMALDEHYDE

The reactions of formaldehyde with both organic and inorganic compounds are well-covered by the articles about formaldehyde, of which the most comprehensive reference is that of Walker (41). Formaldehyde is widely used in industry for production of a variety of different compounds. However, this section has necessarily been restricted to the reactions of formaldehyde-water, formaldehyde-methanol and the polymerisation of formaldehyde because of their relevance to this work.

2.3.1 The Reaction of Formaldehyde with Water

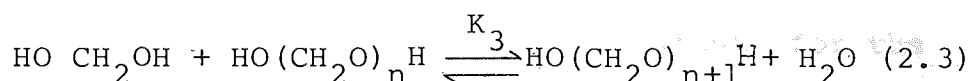
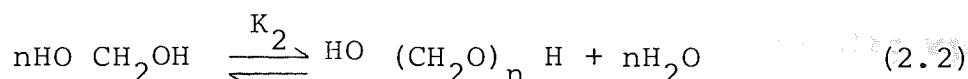
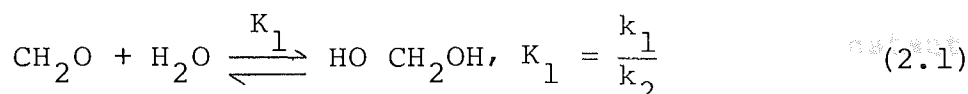
Polymerisation of formaldehyde gas has been observed to occur slowly at room temperature, but it is reported to be stable between 80 to 100°C (42); the liquid monomer polymerises slowly at -80°C, even in the purest form. Rapid polymerisation, which in the extreme can be explosive, is promoted by slight trace of impurities, such as water,

acids and alcohols.

Commercial formaldehyde usually is in the form of aqueous solutions which may contain small amount of formic acid, solid polymeric hydrates and in some cases up to 15 per cent methanol. Formaldehyde is hydrated in aqueous solution and methylene glycol is formed as the monohydrate. Proof of this interpretation of formaldehyde solutions has been found in the fact that, although cryoscopic measurements have shown dissolved formaldehyde is apparently completely monomeric in solutions containing 2 per cent or less dissolved formaldehyde, ultra violet absorption and Raman spectra of these solutions have revealed that the carbonyl grouping ($C:O$) characteristic of the formaldehyde molecule is almost completely absent. The characteristic spectrum of formaldehyde has been obtained by Schou (48) for a solution of formaldehyde in hexane; aqueous solutions gave only a general absorption spectrum which was not differentiated into lines and bands, thus indicating the almost complete absence of the unhydrated formaldehyde in aqueous solution.

Nielsen (49) has shown that almost all the investigators have concluded that formaldehyde solution does not give rise to the fundamental frequencies of the simple formaldehyde molecule. A definite indication of the combined form of formaldehyde has been demonstrated from the study of aqueous formaldehyde solutions by the velocity measurements of ultrasonic waves (50).

In aqueous media, the solution is composed of very small quantities of formaldehyde, monomeric hydrate or methylene glycol $\text{HO CH}_2\text{OH}$ and low molecular weight polymeric hydrates $\text{HO}(\text{CH}_2\text{O})_n\text{H}$ in equilibrium, which may be represented by the following equations (41,43).



where K_1 , K_2 and K_3 represent the equilibrium constants, whilst k_1 and k_2 are the velocity rate constants for equation 2.1.

Methylene glycol is favoured by low concentration of formaldehyde whilst high concentrations favour the polyoxymethylene glycols. The solubility of polymers is decreased with increasing molecular weight and the polymers are precipitated from solution when their concentration exceeds their solubility in the solution media at the corresponding temperature and pressure. Solubility is increased with temperature which also tends to favour an increase in methylene glycol content and a reduction in polymer content.

The hydration of formaldehyde has been found to be rapid. It has been concluded (44) that the lowest velocity constant k_1 for reaction 2.1 is approximately 10s^{-1} at

20 to 25°C. The study of the hydration of formaldehyde by Bell and Evans (44) and by Henaff (45) has shown that $k_2 = 5.1 \times 10^{-3} \text{ s}^{-1}$ at pH of 7 and 25°C. The equilibrium between formaldehyde monomer and methylene glycol in dilute solutions has been demonstrated by Bieber and Trumpler (51), and the approximate value of the equilibrium constant for hydration of formaldehyde to methylene glycol was determined at various temperatures (41). These results were later confirmed by Landquist (52) as a result of polarographic studies. The equilibrium constants for the dehydration of methylene glycol varies from $K_1 = 1 \times 10^{-4}$ to 30.1×10^{-4} over a temperature range of 0 to 64°C, as summarised by Walker (41). A mathematical expression was fitted (43) to this set of chemical equilibrium constant data as a function of temperature. The statistical confidence of the correlation was claimed to be 95 per cent. The parameters were calculated using a least squares fitting technique.

A similar type of expression for the vapour phase reaction was presented by Hall and Piret (53) for both formaldehyde-water and formaldehyde-methanol reactions. Investigations were also carried out by ultra violet spectrophotometer (57) in order to evaluate the thermodynamic parameters. The temperature and pH dependence of rate constants and reaction constants were also reported (58). Iliceto and Bezzi (46) have measured the concentration of aqueous formaldehyde in equilibrium with solid high

molecular weight polymer at moderate temperatures. However, the equilibrium conditions for these heterogeneous reactions are practically never reached under ordinary conditions (41).

Polyoxymethylene glycols are formed by the progressive condensation of methylene glycol. The reaction equilibrium for the polymerisation of methylene glycol are represented by equations 2.2 and 2.3. The values of the reaction constants with $K_2 = 0.33$ for $n \leq 2$ and $K_3 = 0.205$ for $n > 2$ have been experimentally determined by Iliceto and Bezzi (47).

From the reported experimental data (41, 43), a comparison of the rates of reaction in equations 2.1, 2.2 and 2.3 can be made and it can be concluded that reaction 2.1 is much faster than reactions 2.2 and 2.3. Therefore formaldehyde and methylene glycol can be considered as the active chemical compounds in a fresh solution with a moderate formaldehyde content. This assumption can also be supported by studies of the solubility data of the polymers (41).

2.3.2 The Reaction of Formaldehyde with Methanol

Formaldehyde gas is known to be readily soluble in alcohols with the evolution of heat, and on heating the solutions do not give up the formaldehyde. The dissolved formaldehyde in these solutions is thought to be in the form of simple hemiacetals having the formula: $ROCH_2OH$ (41, 53, 83). Analogous to aqueous solutions, these solvates are probably in equilibrium with polyoxymethylene derivatives,

such as $\text{RO}(\text{CH}_2\text{O})_n\text{OH}$ in more concentrated solutions (41). From the available evidence, it has been suggested that the hemiformals or alcoholates of formaldehyde are more stable than the corresponding hydrates and the solution equilibrium are more in favour of the simple hemiformal (41,53,83).

It was noted (54) that when pure dry methanol is added to an approximately equal volume of liquid formaldehyde at -80°C a clear mobile liquid may be first obtained without noticeable heat evolution. However, on standing, a violent reaction takes place, heat is evolved and the mixture solidifies. On warming to room temperature the solid melts and a clear solution is obtained. The approximate heat of solution for gaseous formaldehyde in methanol has been reported by Walker (41) at 23°C as $62.79 \text{ kJ mole}^{-1}$ and approximately the same heat of solution is obtained for the solution of gaseous formaldehyde in water $61.95 \text{ kJ mole}^{-1}$. The heat of polymerisation of formaldehyde has also been found to be of the same order of magnitude. Since the carbonyl linkage in the formaldehyde molecule is saturated with the formation of an $-\text{O}-\text{CH}_2\text{O}-$ grouping in all three molecules, the similarity is explained (41) by the hypothesis that this is the principle factor in determining the quantity of heat evolved.

The affinity of formaldehyde for methanol is also demonstrated by its utilisation as a stabiliser to prevent the precipitation of polymer in concentrated aqueous formaldehyde. The formation of hemiformal has probably

occurred with the consequent lowering of the concentration of the less soluble polyoxymethylene glycols.

Vapour density studies were carried out by Hall and Piret (53,55) who demonstrated that on vaporisation the hemiformal in the alcoholic formaldehyde solutions was less completely dissociated than the methylene glycol from aqueous solution especially at the lower temperatures.

The relative affinity of formaldehyde for water and alcohols has been indicated quantitatively by the data of Johnson and Piret (56) on the partition coefficients of formaldehyde between water and water insoluble alcohols as compared with similar data involving non-polar solvents.

2.4 VAPOUR-LIQUID EQUILIBRIUM OF FORMALDEHYDE SOLUTIONS

Since the discovery of formaldehyde in the 19th century, much data have been published on the vapour-liquid equilibrium of both aqueous formaldehyde solutions and formaldehyde-methanol-water solutions (53,55,59,73). However, large discrepancies have been observed between the published results. These are attributed to the use of many different experimental procedures, equipment and techniques. The phase equilibria in the formaldehyde system are defined by the combination of physical and chemical equilibria which are inter-related such that the variation in any one of these directly affects the other. At a static equilibrium state in a system, both of these concepts would have to be in equilibrium.

Data for the formaldehyde-water system at low pressures (2.66 kNm^{-2}) with boiling points of approximately 20°C were reported by Korzhev and Rossinskaya (64). As the chemical reaction is slower at low temperatures and especially at higher formaldehyde contents, the chemical equilibrium could not have kept up with the boiling rate and therefore true equilibrium would not have been achieved. Thus, the concentration of methylene glycol in the liquid phase would have been found to be greater than the equilibrium values. Thus an increase in the concentration of formaldehyde is caused by an increase in the concentration of methylene glycol (47). The decrease in vaporisation of free formaldehyde at high boiling rates shown by Iliceto (68) and by Bieber and Trumpler (51) can be attributed to the low dehydration of methylene glycol at low temperatures. At higher temperatures, and hence higher pressures, the reaction rate would be increased and as a result the formaldehyde concentration would be increased in the vapour phase.

The effect of pressure on the system was studied by Ledbury and Blair (62) who found that the highest pressure in the system was limited by the instability of formaldehyde. Formaldehyde is decomposed by the Canizzaro reaction, forming methanol and formic acid on heating with water (41). Data at high pressures were presented by Pyle and Lane (66) and experimental values were obtained which differed considerably from those of Farberov and

Speranskaya (70). A copper Othmer equilibrium still was used by Farberov and Speranskaya (70) to study the effect of temperature on formaldehyde decomposition and the vapour liquid equilibrium data for aqueous formaldehyde at different concentrations at 400 kNm^{-2} pressure. The effect of temperature on formaldehyde decomposition was demonstrated in their results.

The vapour-liquid equilibrium data presented by Piret and Hall (55) for aqueous formaldehyde at atmospheric pressure are in quantitative agreement with the earlier data of Auerbach (59). However, an apparent azeotrope at a concentration of 18.25 weight per cent formaldehyde is shown in the data represented by Green and Vener (67).

The consequences of ignoring the reaction kinetics together with the design and operation of the equilibrium stills are emphasised by the difference in the results. In the studies reported by Piret and Hall (55), two methods were employed to obtain the equilibrium data. A different equilibrium still was used in which the vapour composition was measured from small samples of condensate, none of which was returned to the still pot. An Othmer type still in which condensate was returned to the still pot but at a relatively lower rate with respect to the total volume of solution in the still pot was used for the second equilibrium determinations. The slow boiling rate at atmospheric pressure is thought to result in more accurate data in the above experiments. An Othmer type still was

used by Green and Vener (67) in which the distillate was returned to the still pot under conditions which resulted in a slightly higher formaldehyde concentration in the vapour phase than those of the equilibrium vapour.

Recently experimental data have been published by Olsson and Svensson (73) for the vapour-liquid equilibrium of aqueous formaldehyde. They comment that the divergent results obtained by other workers is thought to be due to the boiling methods. As the concentration of formaldehyde in the liquid phase is small and as the rate of dehydration could be less than the rate of evaporation (depending on method, conditions and apparatus), local deficiencies of formaldehyde in the liquid phase could easily be created. Thus the formaldehyde concentration in the vapour phase will be lower than the equilibrium concentrations and superheating will occur. This phenomena was shown to occur by Iliceto (68), who found that the concentration of formaldehyde in the vapour phase was a function of rate of evaporation. Superheating was observed in the experimental data published by Piret and Hall (55). Although some investigators have tried to explain the scattering in data by partial condensation effects, the main reason is thought to be due to the kinetic effect in the liquid phase. Therefore a new procedure was used by Olsson and Svensson (73) to control the rate of vaporisation. A similar experimental method was used to that of Credali et al (71), who determined the vapour pressure of formaldehyde and water above

aqueous formaldehyde solutions at temperatures between 60 and 97°C. In Olsson and Svensson's method nitrogen was bubbled through a formaldehyde solution of known composition and the saturated vapour mixture thereby obtained was analysed for the ratio of formaldehyde to water. Algebraic models were then fitted to the obtained data following the methods given by Prahl (75) and Din (76).

The formaldehyde-water system was also studied by Blazhin et al (213), calculating the activity coefficients of the components without considering the effect of methylene glycol.

The data used in this thesis for the formaldehyde-water system were those of Olsson and Svensson (73) because of its comparative accuracy over all the previous data.

The alcohol-formaldehyde systems have been observed as being apparently similar in many respects to the water-formaldehyde systems except that, as noted by Piret and Hall (55), the alcohol-formaldehyde mixtures are less dissociated than the aqueous solutions. In these solutions formaldehyde is known to be present principally in the form of the simple hemiformal $ROCH_2OH$. In aqueous solutions containing alcohol, it has been noted that the affinity between methanol and formaldehyde is greater than that for formaldehyde and water especially at lower temperatures. The utility of methanol in stabilising aqueous solutions against the precipitation of polymers

can be explained by this phenomenon.

A study of the ternary system of formaldehyde-methanol-water has been made by Green and Vener (67). The systems of formaldehyde-methanol-water and formaldehyde-methanol was studied by Blazhin (213) and the activity coefficients of the components were calculated without considering the products of the reactions of formaldehyde with methanol and water.

2.5 DISTILLATION OF FORMALDEHYDE SOLUTIONS

The behaviour of aqueous formaldehyde solutions on distillation is determined largely by the kinetics of the chemical reactions involved in the hydration and dehydration of formaldehyde. The complicated and unique problems of formaldehyde distillation are governed by the chemical relationships involved in the formaldehyde system. The diverse results obtained by various investigators are explained by these chemical relationships. When solutions are distilled under various conditions the results can be predicted if these chemical relationships are taken into account. Solutions of formaldehyde in nonpolar solvents have been observed to behave normally on distillation since they are not complicated by side reactions.

Reports on the distillation of formaldehyde at low pressures have been made by Korzhev and Rossinskaya (64), Iliceto (68) and Willke (77).

When formaldehyde solutions are subjected to pressure

distillation, formaldehyde is removed in the first fractions and distillates of higher concentration than the original solution are obtained. This effect is illustrated by the data of Ledbury and Blair (69) who employed pressure distillation for the recovery of formaldehyde from dilute aqueous solutions. The concentration of formaldehyde in the distillate fraction was observed to increase with increasing pressure and temperature. As distillation temperatures are increased, the distillation behaviour of aqueous formaldehyde approaches the behaviour of a solution of a volatile gas in water. The effect of higher pressure and temperature on the loss of formaldehyde in distillation through the decomposition of formaldehyde has been studied by Ledbury and Blair (69) and Farberov and Speranskaya (70). A pressure no higher than 300 to 400 kN m^{-2} and temperatures of 130 to 200°C was avoided by Meissner (78) by reducing the exposure of the solution to these conditions in the still.

When formaldehyde distillation is carried out slowly at atmospheric pressure, the expected value for the concentration of formaldehyde in the vapour phase was approached as the reactions involved in vaporisation proceed at a fairly rapid rate at temperatures in the region of 100°C and above (41).

The effect of pH on the distillation of formaldehyde was reported by Iliceto (68). It was concluded that by controlling the pH of the reflux in distillation of aqueous formaldehyde

the concentration of distillate could be increased.

The distillation of formaldehyde-methanol-water mixtures has been published in some patents (80-82), covering the different practical techniques. A distillation study on this system has been reported by Ledbury and Blair (89), giving the proportions of each compound in the distillate of a batch distillation system. According to Hirschberg (79) methanol can be removed from a gaseous mixture containing methanol, formaldehyde and water by distilling the mixture.

2.6 ANALYSIS OF FORMALDEHYDE SOLUTIONS

Numerous chemical and physical procedures involving volumetric, gravimetric and colorimetric methods have been developed for the quantitative or qualitative analysis of formaldehyde solutions. For the quantitative determination of formaldehyde, a wide range of accuracy is obtained for these various techniques. Thus the optimum analytical procedure is best determined by considering the available techniques and the effect of impurities.

In general the analytical techniques can be categorised into physical, chemical and chromatographic methods. Comprehensive details of the physical and chemical analytical methods have been summarised by Walker (41), whilst chromatography has been intensively studied (233-9).

Specific gravity and refractive index measurements are the physical methods used for analysis of pure formaldehyde solutions or solutions containing very small

percentages of impurities. However, methanol is normally contained in most commercial formaldehyde solutions and thus neither of these measurements are sufficient, when used alone, to determine the composition of the solution. By means of a ternary diagram constructed by Natta and Baccaredda (230), both formaldehyde and methanol may be estimated from a solution of the two when both the density and refractive index are known.

The more commonly used chemical methods of analysis are:

1. Sodium sulphite method
2. Alkaline peroxide method
3. Iodimetric method
4. Ammonium chloride method
5. Mercurimetric method
6. Potassium cyanide method
7. Hydroxylamine hydrochloride method
8. Methone or dimedon method

The analysis of impure formaldehyde solutions obtained in connection with the investigation of the mechanism of the combustion of hydrocarbons have been studied by Reynolds and Irwin (232). The different methods available for the chemical analysis of commercial formaldehyde solutions have been investigated by Buchi (231), and it was concluded that only the first five of the mentioned chemical methods are practical in terms of economy, the apparatus and simplicity. The sodium sulphite method was considered to

be the most satisfactory for the analysis of commercial formaldehyde solutions because of its accuracy and simplicity.

In selecting an analytical technique, detailed information concerning the amount of impurity that can be tolerated must be considered because such tolerances vary considerably for different analytical procedures. If the impurity has reacted irreversibly with the formaldehyde, only the free formaldehyde can be determined. If a reversible reaction has taken place, part or all of the combined formaldehyde may be measured.

Further problems can be caused by the measurement of methanol in formaldehyde solutions by chemical methods. The methanol content is measured by estimating the total amount of oxidisable organic material in a solution including formaldehyde. The amount of formaldehyde is then subtracted from the total oxidisable organic material in order to determine the methanol content and a large error can be incurred in the methanol content. However this method cannot be applied if significant quantities of impurities are present since their composition may not be known.

Gas chromatographic separation of formaldehyde has been widely studied and particular attention has been given to the quantitative analysis of the formaldehyde-methanol-water system (233-9). In all of these articles

it has been stated that the polymerisation of formaldehyde in the column must be prevented and this can be achieved by raising the column temperature to over 100°C . However, the choice of stationary phases is restricted by this requirement. Tide on Fluoropak 80 (233), Ethofat 60/25 (235), Polyethylene glycol adipate (236), and sucrose octa acetate (234,235) have been recommended as suitable packings. A synthetic porous polymer such as PORAPAK N (Waters Associates, Inc., Framingham Mass. USA), has been suggested as being a suitable packing. PORAPAK N is reported to be suitable for the analysis of the whole range of formaldehyde solutions (239). A sharp separation of the components, a relatively short retention time together with the constant characteristics of the packing have been achieved over a considerable time period. PORAPAK T has been suggested as a more suitable and specialised packing for the analysis of formaldehyde solutions (240).

The physical measurements used in the analysis of formaldehyde solutions have generally been observed to lead to relatively large experimental errors. Although chemical analytical methods are thought to be more accurate, it has been observed that they are time consuming, especially in the case of analysing for methanol in which the solution must be kept at constant conditions for two to three hours to complete the oxidation step.

However, considerable advantages over both the physical and chemical analytical methods can be achieved by using

gas chromatography as both more accurate and faster results can be obtained. As the time delay between sampling and analysing must be minimised in order to prevent the polymerisation of formaldehyde, gas chromatography using PORAPAK T was selected as the analytical technique.

2. LIQUID EQUILIBRIUM

The increasing role has been played by the design of separation equipment and related control and related processes in important separation processes, which design

vapour-liquid equilibrium, the computer, and the design of systems. The design are based on

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the design of mixtures. On the other hand, the design should be based on the theoretical foundations of interpolation and extrapolation, temperature, pressure, and composition. Because of the large number of multicomponent equilibria, it is necessary to use an efficient technique for the design of experimental data with a significant number of data and a significant number of data. However, the design of

3. VAPOUR-LIQUID EQUILIBRIUM

3.1 INTRODUCTION

In recent years an increasing role has been played by electronic computers in the design of separation equipment as used in the chemical, petroleum and related industries. Distillation is one of the important separation processes. Numerous articles have been published which present detailed computer methods for use in the design of multicomponent distillation towers.

Calculations for the prediction of vapour-liquid equilibrium data are an integral part of the computer program for the design of distillation columns. The calculation techniques are based on generalised methods, as it would not be practicable to construct different methods for any individual system. Thus, generalised techniques must be considered for calculating vapour-liquid equilibrium for multicomponent mixtures. Only a limited amount of experimental information should be needed for the techniques which should be based on theoretical foundations in order to be reliable for interpolation and extrapolation with respect to temperature, pressure and composition of the system. Because of the large number of variables which determine multicomponent equilibria, these variables must be used with an efficient technique to represent a large amount of experimental data with a small number of theoretically significant functions and parameters. This can be achieved by utilising thermodynamic analysis of the equilibria. However, more simple

methods have been developed, mainly using numerical techniques, to fit polynomial correlations to the existing experimental data (75), or the distribution coefficients.

Thermodynamically, a system is said to be in equilibrium when a reversible system has no tendency to change. Hence the entropy of the system would be unchanged and the difference in entropy would be zero. An equilibrium system is better defined by using the concept of chemical potential. For two phases in equilibrium the chemical potential of one component in phase 1 is equal to the chemical potential of the same component in phase 2.

However, a physically more meaningful quantity, equivalent to the chemical potential, can be obtained by a simple transformation. The parameter obtained from this transformation is called the fugacity. The fugacity of a constituent in multicomponent equilibria would be equal in the two phases. If the fugacity of each phase is substituted in terms of measurable parameters such as liquid and vapour phase concentrations, pressure and temperature, the general and well known equation for the equilibria is obtained. The correlations and procedures for the derivation of these thermodynamic relationships are well known and can be found in most of the classical thermodynamic text books (145-8). The final expression is obtained in terms of pressure, fugacity coefficient,

activity coefficient and vapour and liquid mole fractions. The vapour and liquid mole fractions are quantities of physical reality which appear in the equilibrium relationships. The quantities are not explicit, where each quantity is defined in terms of other quantities. The fugacity coefficients are functions of composition, temperature and pressure.

3.2 LITERATURE SURVEY

3.2.1 Liquid Phase Model

Each of the thermodynamic concepts appearing in the equilibrium expression must be analytically related to more realistic parameters such as temperature, pressure and composition. Numerous articles have been published on this subject and some have dealt with the techniques of solution for the resulting equation. In other articles, analytical models have been proposed to correlate the activity coefficient, fugacity coefficient and equations of state in terms of temperature, pressure and composition. A critical review of these methods has been made by Smith (162). Several correlations have been developed to express the activity coefficient in terms of composition. Two of the earliest methods were developed by Van Laar (149) and Margules (150). Some experimental constants are contained in each correlation. For example, the Van Laar constants are assumed to depend only on the temperature and have the units of energy. A different approach was

introduced by Wohl (151) who showed that many of the common empirical equations could be derived from a generalised treatment, by expressing the excess Gibbs energy function as a polynomial expansion in the effective volume fractions. The resulting equations are commonly known as Redlich, Kister type expansions (152).

A new approach was made by Wilson (153) to relate the excess Gibbs energy function to composition by introducing the local mole fraction concept. A different value for the local mole fraction from the overall value of mole fraction in the immediate surrounding of a molecule is introduced in this approach. Four values can be determined in a binary mixture for the local mole fractions and only two of these values are independent. The local mole fractions were related by Wilson to the overall mole fractions, by assuming a Boltzman type expression and by substituting local volume fractions for overall volume fractions in the Flory-Huggins equation (243,244). The final expression derived by Wilson could easily be applied to a multicomponent system, provided that the experimental data for every possible binary system are known.

Several important advantages over the earlier models are contained in the Wilson equation. A reasonable approximation can be made by assuming that the characteristic energy constants in the Wilson equations are independent of temperature. For normal accuracy the assumption is valid for approximately twenty degrees

centigrade intervals. Also highly asymmetric systems, such as solution of polar or associating components in non-polar solvents can be correlated by the Wilson equation. However, the principal advantage of the Wilson equation is that it can be readily extended to multicomponent mixtures from the data of the corresponding binary systems.

The Wilson equation cannot be applied to partially miscible liquid mixtures. When the correlation is substituted into the equations of thermodynamic stability for a binary system no parameters can be found to indicate the existence of two stable liquid phases.

The local mole fraction concept has been combined by Renon and Prausnitz (160) with Scott's (166) two liquid theory of mixtures, to derive the NRTL (Non-random Two Liquid) equation. The NRTL equation can be applied to most of the partially miscible systems as well as the multicomponent systems, if the parameters of corresponding binary systems are known.

The NRTL equation has been modified by Asselineau and Renon (167) in order to increase the temperature range over which the equation can be applied. A linear function was used for the temperature dependence of the parameters. Thus the integral heat of mixing could be included and the resulting modification gave improved accuracy.

3.2.2 Vapour Phase Model

The vapour phase is modelled by the equation of state. Many empirical equations of state have been proposed, each relating pressure, molar volume and temperature to allow for imperfect gas behaviour. These equations may be explicit in either pressure or the volume, where the pressure or volume is expressed in terms of other variables. The perfect gas is characterised by the equation of state

$$z = \frac{PV}{RT} = 1 \quad (3.1)$$

Significant deviations from this equation may be shown by real gases even at low pressures. One of the more simple models for the equation of state for real gases is the one parameter equation of state in the form of equation 3.2.

$$P(V - B) = RT \quad (3.2)$$

where B is an empirical constant representing nonideality in the volume of the gas.

Larger deviations from the gas laws can be represented by equations containing more than one constant, such as the Van der Waal equation. The number of constants is generally proportional to the accuracy of the model.

The Van der Waal, Dieterici and Berthelot equations are three of the classical equations which have received considerable attention. Although the real gas behaviour

over the whole pressure and temperature range is not entirely correlated by these three equations a gas-liquid critical point is provided by these equations in the phase diagram. The solution of those equations in terms of critical pressure, volume and temperature can be used to define the constants in the equations and therefore each equation can be written in the form of reduced parameters.

The models proposed by Clausius (176) and Wohl (177) are the well known three parameter equations of state which are based on the Van der Waal equation. The Clausius equation has since been modified by Elshayal and Lu (178) by considering temperature dependent constants for the equation.

The negative curvature at low densities, positive curvature at intermediate densities and negative curvature at high densities can be predicted by only some of these equations and thus the observed behaviour of the gases is not well predicted by the various equations of state. One of the equations which shows all three characteristics is that developed by Benedict, Webb and Rubin (BWR) (179-82) which contains eight empirical constants. This equation, like many other equations (183-9), is based on a hard sphere molecular model.

It has been claimed that (190) the equation of state for real gases is best represented over a wide temperature and pressure interval, by the virial equation of state, which contains a series expansion of the compressibility

factor. Further it has been claimed that (191-2) the virial equation has a sound theoretical foundation for representing the properties of pure and mixed gases when it has been truncated after the third term. Some investigators (193-6) have shown that the chemical theory of gas imperfection leads to an equation of state of the virial form. Methods for estimating second and third virial coefficients of mixtures have been presented (197-202) and a considerable amount of theoretical knowledge and experimental data have been determined for the second virial coefficient (190), whilst little information has been obtained for the third and higher order virial coefficients. However, the virial equation of state can only be used for low or moderate pressures and densities. In principle, the equation can be used for high pressures but at such pressures, a large number of virial coefficients are required to give an adequate correlation. However, at moderate densities the third and higher virial coefficients may be safely neglected.

For the high pressure region, the data are more accurately correlated by the Redlich-Kwong (203) equation of state. The Redlich-Kwong equation has been modified by Chaudron, Asselineau and Renon (204) and this equation can be applied for computer calculations of high pressure systems. A quadratic combination rule was suggested by Redlich and Kwong for the parameters in their equation of state. A different correlation was presented by Wiswanath

et al (205) for the constants, which was modified by Zudkevitch and Joffe (206) and Robinson and Jacoby (207) by introducing a mixture characteristic parameter.

By assuming an equation of state for a system, the fugacity coefficient of the components could easily be calculated using the original thermodynamic relationship derived by Beattie (208). A working equation for the calculation of the fugacity coefficient would be obtained by substituting the equation of state into Beattie's equation. Depending on the type of equation of state, different correlations could be obtained for the fugacity coefficient of the system.

3.2.3 Vapour-liquid Equilibrium of Reacting Systems

The phase equilibrium data obtained by different investigators has failed to meet the criteria of the thermodynamic consistency tests despite careful experimental techniques. The existence of an unrecognised chemical reaction may be put forward as one explanation for such a discrepancy. Once all the chemical species have been identified, the data can be shown to be thermodynamically consistent. Several investigations concerned with vapour-liquid equilibrium for systems accompanied by chemical reaction has been reported in the literature (209-12), and the basic principles of the combined chemical and phase equilibria have been reported by Null (146).

The tendency for certain components to associate

in the vapour phase has been cited as a frequent cause of an apparent anomaly in phase equilibria data. This tendency is known to be especially strong in organic acids, hydrogen fluoride and some aldehydes.

The liquid phase is generally considered to consist of molecules exhibiting a certain degree of order and often moving in clusters rather than in individual random movements of molecules. An ideal solution is defined to be when a molecule is able to leave or enter such clusters of a different species of molecules just as easily as it does with its own cluster. In general, some of the liquid phase association is accounted for by the activity coefficients. However, in some systems an identifiable chemical compound that only exists in the solution is created by the presence of strong association. In formaldehyde-water solution a third component, polymethylene glycol, is formed through the existence of strong association. Any attempt to correlate the phase equilibrium of this system by using the classical equations for activity coefficients and ignoring the existence of the third component will fail. Usually, the data for most systems can be fitted by assuming the appropriate chemical association. A theory was proposed by Dolezalek (214) that all solutions were in fact ideal and any non-ideality resulted from failure to identify the appropriate associating component. Even if this assumption was correct, the approach cannot be generally applied and should be used

only in specific cases where the data and appropriate chemical tests indicate that a strong associating compound actually exists.

The concept of liquid phase association has been used by Wiehe and Bagley (215) to derive an equation for activity coefficients in systems not readily fitted by the classical equations. They assumed that the Gibbs free energy of mixing of an associating compound with a non-associating compound is given by the Flory Huggins model, that all the associated complexes have the same density and that the chemical equilibrium constant is independent of the number of associated molecules. An equation for the activity coefficients of strongly associating liquids was derived based on these assumptions.

Many types of dissociating components are known to exist in liquid solutions which directly affect the phase equilibrium. In the case of ionised molecules an extra constraint must be observed and that is the overall charge of neutrality of the solution.

Despite the apparent usefulness of such methods, generalised methods of solution for a rigorous model have not been developed. The available methods for calculation of chemical equilibria has been reviewed by Zeleznik and Gordon (216). In general it was observed that published methods of calculating the equilibrium composition of a chemically reacting system, fell into one of two categories.

In the first category, the chemical equilibrium and material balance equations are solved algebraically whilst in the second category, developed by White et al (217), the free energy of the system was minimised. The first method can be applied for data correlation and process simulation whilst the second is more suitable for large systems and for estimation.

The simultaneous chemical and phase equilibrium were solved by Sanderson and Chien (218) by using the chemical equilibrium and material balance equations for the chemical side of the problem combined with the thermodynamic expression for the phase equilibria. The problem was then formulated into an unconstrained, non-linear problem which could be solved numerically.

A technique of calculation for the mixtures containing a substance which associates to a dimer has been suggested by Marek and Standart (219). They distinguished between the stoichiometric and true mole fraction of each of the components present in a system. Thus an expression was derived to relate each of the mole fractions, and the appropriate physical concepts using the existing and available data.

A calculation procedure was presented by Chueh (220) for the activity coefficients of multicomponent solutions containing formic acid, acetic acid, formaldehyde, acetaldehyde and water, using a modified version of the

Wilson equation. Although many simplifying assumptions were made the results were an improvement on the existing correlations.

Some of the above-mentioned methods have been applied by Gibson Robinson (170) and Davies (89) for the strongly associating systems of acetic acid-water, acetic acid-toluene and ethyl alcohol-butyl acetate.

3.2.4 Parameter Fitting

The Wilson parameters for binary systems are usually estimated by one of the general purpose non-linear estimation computer programs through minimisation of the sum of squares of the deviations between the predicted and observed values of composition, pressure or temperature of the system. A large number of different methods which depend on the number of available experimental points or the regression techniques have been published. The articles most related to this work are those of Nagahama et al (221) and Cheng et al (222).

If only one set of data is available, the activity coefficients can be derived using a thermodynamic relationship. A function can then be calculated by substituting for one of the constants in the Wilson equation. A pair of constants would be obtained from the solution of the resulting equation with the experimental data. Usually scattered constants are obtained from the application of this method to each set of data points.

If two experimental points are available, the constants can easily be calculated by the solution of two simultaneous equations.

Generally the activity coefficients cannot be represented for the entire concentration range using the parameters determined by the methods previously mentioned. Usually the least squares fitting technique is used to determine the values of the constants from all the experimental data.

The more common methods which are being used are:

1. The non-linear squares method (223).
2. The gradient search method (224, 225, 229).
3. The pattern search method (226).
4. The complex search method (227-8).

Marquardt's method (225) was used for the estimation of the parameters in this research.

3.3 PHASE EQUILIBRIA

3.3.1 Thermodynamics of Vapour-Liquid Equilibrium

Thermodynamic equilibrium is defined as the final point of a reversible process and from this definition the condition of the equilibrium can be expressed mathematically. Thus no change would be obtained in temperature, pressure and conditions if a system was at its equilibrium state. Subsequently the change in free energy, work, heat and entropy of the system under equilibrium would be zero.

If a system consisting of two phases- (e.g. vapour and liquid of a pure substance) is considered, it can be shown thermodynamically that the free energy of the components in the two phases are equal and thus the chemical potentials in the two phases would also be equal.

The chemical potential is defined as the molar internal energy of the component in a phase. For a closed system at a constant pressure and temperature, the chemical potential would be equal to the molar free energy of the component. Since a system in phase equilibrium is a closed system at constant pressure and temperature, the chemical potential could be defined in terms of the free energy

$$d\mu_i = \left(\frac{\partial G_i}{\partial n_i}\right)_{P,T} \quad (3.3)$$

An immediate equivalent in a physical sense cannot be suggested for the chemical potential and so it is desirable to express the chemical potential in terms of an auxiliary function which might be more easily identified with physical reality.

For a perfect gas, the chemical potential is defined as a linear function of the logarithm of its pressure. In the case of a non-ideal gas a fictitious pressure is defined as the fugacity, to which the chemical potential of the gas bears the same linear relationship. Physically, the fugacity can be conveniently thought of as a thermodynamic pressure because for an ideal gas the fugacity would be equal to ^{the} vapour pressure of the gas. The

relationship between the fugacity and the chemical potential is given by the equation 3.4.

$$\mu_i - \mu_i^o = RT \ln \frac{f_i}{f_i^o} \quad (3.4)$$

where either μ_i^o or f_i^o is arbitrary. However both parameters cannot be chosen independently, because when one is chosen, the other is fixed and these conditions are called standard state. The relationship between the fugacity and the chemical potential is the starting point for the transformation of pure thermodynamics to the physical variables. The transition from pure thermodynamics to the theory of inter-molecular forces is helped by the concept of fugacity.

Similar types of equation have been defined for the liquid phase, where the chemical potential of the liquid phase is related to the liquid phase concentration. For the case of a non-ideal liquid, the activity coefficient is introduced as a correction factor.

In a system where two phases are in equilibrium, equation 3.4 could be applied to describe the equilibrium

$$\mu_i^V - \mu_i^{oV} = RT \ln \frac{f_i^V}{f_i^{oV}} \quad (3.5)$$

$$\mu_i^L - \mu_i^{oL} = RT \ln \frac{f_i^L}{f_i^{oL}} \quad (3.6)$$

where superscripts V and L refer to the phases V and L.

If the standard state for the two phases is the same,

$$\mu_i^{oV} = \mu_i^{oL} \quad (3.7)$$

$$f_i^{oV} = f_i^{oL} \quad (3.8)$$

A new form of the fundamental equation of phase equilibrium will be given by the substitution of equations 3.7 and 3.8 into equation 3.5 and 3.6.

$$f_i^V = f_i^L \quad (3.9)$$

A binary mixture is a simple form of phase equilibria, where the concentration of the two components in the phases have to be determined at equilibrium. A simple relationship has to be derived to describe the distribution of the components between the phases. This relationship can be obtained in the form of an equation relating the mole fraction of a component in the liquid phase to the mole fraction of the same component in the vapour phase. Equation 3.9 could be applied to this system, where the superscripts V and L refer to the vapour and liquid phases respectively and subscript i refers to component i in the binary mixture.

Two simplifying assumptions can now be made to equation 3.9. The first assumption to be made is that the vapour phase fugacity at constant pressure and temperature is proportional to the mole fraction of

component i in the vapour phase, Y_i . In equation 3.10, Y_i is the mole fraction of component i in the vapour phase and $f_{\text{pure } i}^V$ is the fugacity of pure component i as a liquid at the temperature and pressure of the system.

$$f_i^V = Y_i f_{\text{pure } i}^V \quad (3.10)$$

The second assumption to be made is that the liquid phase fugacity at constant temperature and pressure is proportional to the mole fraction of component in the liquid phase, X_i .

$$f_i^L = X_i f_{\text{pure } i}^L \quad (3.11)$$

In equation 3.11 $f_{\text{pure } i}^L$ is the fugacity of pure component i as a liquid at the temperature and pressure of the system. The ideality in both the liquid and vapour phases is indicated by these two assumptions. Equation 3.10 and 3.11 can be substituted into equation 3.9 to give the new form of the equilibrium equation.

$$Y_i f_{\text{pure } i}^V = X_i f_{\text{pure } i}^L \quad (3.12)$$

For an ideal gas the fugacity of a pure component would be equal to the pressure of the system.

$$f_{\text{pure } i}^V = P \quad (3.13)$$

The effect of pressure on the fugacity of a condensed phase is assumed to be negligible at moderate pressures.

The vapour in equilibrium with pure liquid i at temperature T is an ideal gas; therefore

$$f_{\text{pure } i}^L = p_i^S \quad (3.14)$$

where p_i^S is the saturation or the vapour pressure of pure liquid i at temperature T . Raoult's rule can be obtained from the substitution of equations 3.13 and 3.14 into equation 3.12

$$y_i P = x_i p_i^S \quad (3.15)$$

However, the application of this equation is limited because of the severe simplifying assumptions which have been made. In general more complex relationships should be applied to overcome the assumption of ideality in the liquid and vapour phases, but the procedure for the substitution will remain the same.

The desired relationship between the fugacities and experimentally accessible quantities is facilitated by two auxiliary functions ϕ and γ . The vapour phase fugacity is related by the fugacity coefficient ϕ to the mole fraction and total pressure and is defined by equation 3.16

$$\phi_i = \frac{f_i^V}{y_i P} \quad (3.16)$$

The liquid phase fugacity is related by the activity coefficient to the mole fraction and to a standard state fugacity f_i^{OL} and is defined by equation 3.17.

$$\gamma_i = \frac{f_i^L}{X_i f_i^{oL}} \quad (3.17)$$

When equations 3.16 and 3.17 are substituted into equation 3.9 for the vapour and liquid phases fugacity, the more general equation for equilibria can be obtained.

$$\phi_i Y_i P = \gamma_i X_i f_i^{oL} \quad (3.18)$$

The previous assumptions can be overcome by employing an equation of state for the vapour phase, which represents the behaviour of real gases. The non-ideal liquid phase is considered by the introduction of the activity coefficient.

Although equation 3.18 can be applied to non-ideal liquid and vapour phases, it is not sufficient for the systems where a chemical reaction occurs in the system, unless the new components which are produced from the chemical reaction are considered and accounted for. The change occurring in systems with chemical reaction or in systems with a degree of association can be represented generally by two different methods. In the first technique, the effect of the chemical reaction on the change of the mole fractions in both the vapour and liquid phases is considered. The effect of the chemical reaction should then be considered for the rest of the parameters such as fugacity, activity coefficients, partial pressures and vapour pressures. The components resulting from the chemical reaction must also be included. In the second method, the basic thermodynamic relationships such as the

free energy function are modified to include the effect of the chemical reaction. The chemical potential for each component is entered in an equation similar to the equation representing the chemical reaction and thus an overall relationship for the phase and chemical equilibria is formed (146, 218, 212).

3.3.2 Virial Equation of State

The need for a reliable equation of state for the gas mixtures is reflected in the calculation of fugacities for components in a gaseous mixture. Once such an equation of state has been selected, the fugacities can be determined by straightforward computation.

The different equations of state have been discussed in section 3.2.2. Almost all the proposed equations are essentially empirical in nature. The empirical equations of state are based on a number of arbitrary assumptions which are not generally valid. The constants in an empirical equation of state for a pure gas have only approximate physical significance. Therefore the application of these equations to a mixture of gases would be difficult if the rules for expressing the constants of the mixture in terms of the constants of the pure components were not defined. As a result more assumptions would have to be introduced into these relationships. Furthermore, good results may be obtained for one system using an equation of state with a set of mixing rules but the same equations and rules may give a poor result

for another system.

The non-ideality of a gas is reflected by the constants which appear in a gas phase equation of state. In order to establish composition-dependent constants, it is important that the constants in an equation of state have a clear physical significance. The virial equation of state for gases has a sound theoretical foundation and is free from arbitrary assumptions. In the virial equation, the compressibility factor is expressed as a power series in terms of the reciprocal molar volume. This equation is also referred to as the pressure explicit form of the virial equation,

$$Z = \frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \dots \quad (3.19)$$

where the constants B , C and D are the second, third and fourth virial coefficients respectively. The virial coefficients are defined as being independent of pressure or density and for a pure component they are a function of temperature. The advantage of this equation is that the constants are related to the intermolecular potential and that for a gas mixture the constants can exactly be defined.

$$B = \text{Limit}_{\rho \rightarrow 0} \left[\frac{\partial Z}{\partial \rho} \right]_T \quad (3.20)$$

$$C = \text{Limit}_{\rho \rightarrow 0} \left[\frac{\partial^2 Z}{\partial \rho^2} \right]_T \quad (3.21)$$

The volume explicit form of the virial equation, given

by the equation 3.22, is defined as a similar type of equation, where in this case, the constants are independent of pressure or density, but for a gas mixture they are a more complex function of composition.

$$Z = \frac{PV}{RT} = 1 + B'P + C'P^2 + D'P^3 + \dots \quad (3.22)$$

Each of the constants in these equations can be expressed in terms of the constants in the other equation, thus facilitating the change of one form of equation to another. The pressure explicit form of the equation is thought to be superior because a wider range of densities can be covered by this equation than by the volume explicit equation.

For many different gases it has been reported (190) that equation 3.19 when truncated after the third term gives a good representation of the system up to approximately half the critical density. From half the critical density to the critical density, the representation has been found not to be accurate. For higher gas densities, the virial equation is not widely used because the high density systems require the use of higher order virial coefficients which are not well defined. However, the virial equation can be applied to moderate density systems which are commonly encountered in many vapour-liquid problems.

No inter-molecular forces are detected in an ideal gas. The inter-molecular forces detected in real gases are observed to be proportional to the distance between the molecule of the gas. Thus low inter-molecular forces

will be found in low density gases due to the larger distances between the molecules and therefore the gas is closer to the ideal gas state in its behaviour. These deviations from ideal behaviour which may result from collisions or interactions between two molecules at any given instant are taken into account by the second virial coefficient. The effect of collisions of three molecules is taken into account by the third virial coefficient. The physical significance of the higher virial coefficients may be taken to follow in an analogous manner.

3.3.2.1 Correlations for Virial Coefficients

For pure non-polar gases, a good approximation for the second virial coefficient has been given by Pitzer and Curl (197, 241) based on a three parameter theory of corresponding states.

$$\frac{P_{ci} B_{ii}}{R T_{ci}} = F_0(T_r) + \omega_i F_1(T_r) \quad (3.23)$$

The acentric factor ω_i for the component i in the gas phase is defined by,

$$\omega_i = - \log_{10} \left(\frac{P_i^s}{P_{ci}} \right) - 1 \quad (3.24)$$

P_{ci} and T_{ci} are the critical pressure and temperature of component i respectively. The empirically determined functions $F_0(T_r)$ and $F_1(T_r)$ are a function of the reduced temperature and are defined by

$$F_0(T_r) = 0.1445 - \frac{0.33}{T_r} - \frac{0.1385}{T_r^2} - \frac{0.0121}{T_r^3} \quad (3.25)$$

$$F_1(T_r) = 0.073 + \frac{0.46}{T_r} - \frac{0.50}{T_r^2} - \frac{0.0073}{T_r^8} \quad (3.26)$$

For polar gases, different correlations based on an extended corresponding state theory have been presented by Prausnitz et al (191) in the form of

$$\frac{P_{ci} B_{ii}}{R T_{ci}} = F_0(T_r) + \omega H_i F_1(T_r) + F_2(\mu_r, T_r) + \eta_i F_3(T_r) \quad (3.27)$$

where ωH_i stands for the acentric factor of the polar component's homomorph. A homomorph of a polar molecule is a non-polar molecule, having approximately the same size and shape. The function $F_2(\mu_r, T_r)$ is related to the reduced dipole moment (μ_r) of the component:

$$F_2(\mu_r, T_r) = -5.23722 + 5.665807 \ln \mu_r - 2.133816 (\ln \mu_r)^2 + 0.2525373 (\ln \mu_r)^3 + \frac{1}{T_r} [5.76977 - 6.181427 \ln \mu_r + 2.28327 (\ln \mu_r)^2 - 0.2649074 (\ln \mu_r)^3] \quad (3.28)$$

and

$$\mu_r = \frac{10^5 \mu_{di}^2 P_{ci}}{T_{ci}^2} \quad (3.29)$$

where μ_{di} is the dipole moment of component i in debye. The tendency of a component to associate is reflected by the association constant η . The association function $F_3(T_r)$ is given by

$$F_3(T_r) = \exp(6.6(0.7 - T_r)) \quad (3.30)$$

The polar contribution in equation 3.27 is used below a reduced temperature of 0.95 but is neglected at higher temperatures. For values of μr less than 4.0, equation 3.29 is not applicable and the polar contribution should be ignored.

The definition of cross correlation constants B_{ij} , where i and j are different, are required for the extension of Pitzer and Curl's correlation to mixtures. For cases where i and j are both non-polar gases, equations 3.23-6 can be applied by replacing P_{cij} for P_{ci} , T_{cij} for T_{ci} and ω_{ij} for ω_i . The approximate form of the physical variables can be obtained by using the following relationships.

$$T_{cij} = (T_{ci} T_{cj})^{1/2} \quad (3.31)$$

$$\omega_{ij} = \frac{1}{2}(\omega_i + \omega_j) \quad (3.32)$$

$$P_{cij} = 4T_{cij} \left[\frac{P_{ci} V_{ci}}{T_{ci}} + \frac{P_{cj} V_{cj}}{T_{cj}} \right] / (V_{ci}^{1/3} + V_{cj}^{1/3})^3 \quad (3.33)$$

Good results are obtained for those mixing rules when components i and j have similar molecular size and volatility. When components i and j are not similar, an empirical modification of the mixing rules may be required.

For cases where i is a polar molecule and j is a non-polar molecule, equations 3.23-6 are used for B_{ij} , equation 3.31 is used for T_{cij} , equation 3.34 for ω_{ij}

and equation 3.33 for P_{cij} .

$$\omega_{ij} = \frac{1}{2}(\omega_{H_i} + \omega_j) \quad (3.34)$$

When components i and j are both polar, equation 3.27 is used for B_{ij} where T_{ci} is replaced by T_{cij} , P_{ci} by P_{cij} , ω_{H_i} by $\omega_{H_{ij}}$ and η_i by η_{ij} . The reduced dipole moment μ_r is given by

$$\mu_r = \frac{10^5 \mu_{d_i} \mu_{d_j} P_{cij}}{T_{cij}^2} \quad (3.35)$$

The values of η_{ij} and $\omega_{H_{ij}}$ can be calculated from equations 3.36 and 3.37.

$$\eta_{ij} = \frac{1}{2}(\eta_i + \eta_j) \quad (3.36)$$

$$\omega_{H_{ij}} = \frac{1}{2}(\omega_{H_i} + \omega_{H_j}) \quad (3.37)$$

Only approximate values are given by the mixing rules mentioned and the rules should be used when there is no other information available. The most important advantage of the virial equation of state for its application to phase equilibria problems is that it can be extended directly to mixtures which require no arbitrary assumptions.

In a pure gas the chemical identity of each of the interacting molecules can be taken as being the same. In a mixture however, various types of two molecule interactions can be applied depending on the number of components which are present. For a binary mixture

consisting of components i and j , three types of interaction, $i-i$, $j-j$ and $i-j$ can be applied where for each of these interactions there is a corresponding second virial coefficient.

The second virial coefficient of a mixture is given by equation 3.38. The second virial coefficient of the mixture can be obtained using equation 3.38, which is a function of the second virial coefficients of all the possible binary systems,

$$B_{\text{mixture}} = \sum_{i=1}^m \sum_{j=1}^m Y_i Y_j B_{ij} \quad (3.38)$$

where the subscripts i and j refer to the component number in a system of m components. The third virial coefficient of a mixture is related to the various C_{ijk} coefficients which take into account interactions between the three molecules i , j and k . A generalised form of the equation for third virial coefficient for a mixture of m component is given by equation 3.39.

$$C_{\text{mixture}} = \sum_{i=1}^m \sum_{j=1}^m \sum_{k=1}^m Y_i Y_j Y_k C_{ijk} \quad (3.39)$$

3.3.3 Fugacity Coefficient

The fugacity of a component in the vapour phase is related by the fugacity coefficient to the total pressure and mole fraction of the same component where the fugacity coefficient is a function of temperature, total pressure

and composition of the vapour phase. Rigorous thermodynamic relationships have been derived by Beattie (208) to express the fugacity coefficient in terms of the physical variables of the system. The fugacity coefficient can be expressed for the independent variables V and T and for the independent variables P and T by equations 3.40 and 3.41 respectively.

$$\ln \phi_i = \frac{1}{RT} \int_0^P \left[\left(\frac{\partial V}{\partial n_i} \right)_{T,P,n_j} - \frac{RT}{P} \right] dP \quad (3.40)$$

$$\ln \phi_i = \frac{1}{RT} \int_V^\infty \left[\left(\frac{\partial P}{\partial n_i} \right)_{T,P,n_j} - \frac{RT}{V} \right] dV - \ln Z \quad (3.41)$$

As the volume series form of the virial equation of state is being used, equation 3.41 would be the appropriate form of the fugacity coefficient.

If the vapour mixture consists of an ideal gas, the integral in equation 3.40 and 3.41 would be zero and Z , the compressibility factor would equal unity for all compositions, and ϕ_i would be equal to unity for any component. At low pressures up to 100 kN m^{-2} , the fugacity coefficient is often assumed to equal one, but at moderate pressures of up to approximately 1000 kN m^{-2} , the fugacity coefficient is often significantly different from unity.

A basis for the calculation of the fugacity coefficient in terms of the pressure and temperature of the system can be obtained by substituting the variables from the virial equation 3.19 into equation 3.41. A

working equation for the fugacity coefficient can be obtained by further substitution for the virial coefficients

$$\ln \phi_i = \frac{2}{V} \sum_j^m Y_j \cdot B_{ij} + \frac{3}{2V^2} \sum_j^m \sum_k^m Y_j \cdot Y_k C_{ijk} + \dots - \ln Z_{\text{mix}} \quad (3.43)$$

where V is the molar volume of the gas.

When the third and higher order virial coefficients are neglected, the fugacity coefficient is given by

$$\ln \phi_i = \frac{2}{V} \sum_j^m Y_j \cdot B_{ij} - \ln Z \quad (3.43)$$

3.3.4 Activity Coefficient

The definition of the activity coefficient has been given in Section 3.3.1. The activity coefficient can be clearly defined when the liquid phase standard state fugacity is specified. The definition of the standard state fugacity is arbitrary therefore the standard state can be chosen for convenience. The system temperature should be selected as the temperature at which the standard state fugacity is chosen.

Certain conventions have been adopted in the choice of a standard state fugacity. These conventions have been adopted as a result of two important considerations:

- (a) The necessity for a thermodynamic definition of non-condensable gases dissolved in a liquid phase.
- (b) The relationship between the activity coefficients

given by the Gibbs-Duhem equation. The activity coefficient is normalised by the first of these conventions and the activity coefficient is defined by the second convention in terms of physical variables.

Specification of the state where the activity coefficient is unity can be obtained by normalisation of the activity coefficient,

$$\text{thus } \gamma_i \rightarrow 1 \quad \text{as} \quad X_i \rightarrow 1$$

The fugacity for each component is then defined by the product of the mole fraction and the standard state fugacity as the composition of the solution approaches that of the pure component. Therefore the standard state fugacity would be equal to the pure liquid of that temperature. The same can be applied to all the condensable components in the mixture. Normalisation of the activity coefficient is said to follow the symmetric convention. This method of normalisation cannot be applied when a supercritical component is present in the system. A supercritical component in the system is defined as a component whose critical temperature is close to or below the system temperature. If the system temperature is very close to or slightly above the critical temperature of one or some of the components, some estimates of the liquid properties could be provided by extrapolation of these properties to high temperatures. The non-condensable component is then

assumed to be a hypothetical liquid.

The concept of hypothetical liquids cannot usefully be applied for highly non-condensable components because the extrapolation of pure liquid properties is so excessive as to lose all physical significance. Therefore a different normalisation procedure has been used for non-condensable components, namely

$$\gamma_i \rightarrow 1 \quad \text{as} \quad X_i \rightarrow 0$$

According to this definition, the fugacity of component i becomes equal to the product of the mole fraction and the standard state fugacity of component i when component i is infinitely dilute. The concentration region where the activity coefficient of a dilute component is equal to unity is called the ideal dilute solution or the Henry's law region. The characteristic constant for the ideal dilute solution is the Henry's law constant and is defined by

$$H = \lim_{X_i \rightarrow 0} \frac{f_i^L}{X_i} \quad (3.44)$$

where H is Henry's constant for a non-condensable component, f_i^L and X_i are the liquid-phase fugacity and mole fraction of the non-condensable component i . As the normalisation of condensable components is different from the normalisation of the systems containing condensable and non-condensable components, it is called an unsymmetric convention.

By definition, the standard state fugacity of a non-

condensable component is set equal to Henry's constant which depends not only on temperature but also on the solvent or the condensable component. Some difficulty is caused by this assumption in multicomponent systems where the solvent is not a pure component. This problem is solved by assuming the condensable phase which is a mixture of more than one component, to be a pure reference solvent.

The equation can be summarised as follows. For condensable components

$\gamma_i \rightarrow 1$ as $x_i \rightarrow 1$ and $f_i^{OL} = \text{fugacity of pure liquid}$
and for the non-condensable components

$\gamma_i \rightarrow 1$ as $x_i \rightarrow 0$ and $f_i^{OL} = H_i$ (in pure reference solvent)

3.3.5 Gibbs-Duhem Equation

In a mixture, the partial molar properties of the components are related to one another by the Gibbs-Duhem equation. At constant pressure and temperature the equation would be

$$\sum_i x_i dU_i = 0 \quad (3.45)$$

where $m_i = \frac{\partial U_i}{\partial n_i}$ (3.46)

and m_i is any partial molar property.

Equation 3.45 can be used for both ideal and real solutions.

This equation can be applied for two important situations. In the absence of complete experimental data on the properties of a mixture, the Gibbs-Duhem equation can be used to calculate the additional properties. Secondly, if the experimental properties are available, the Gibbs-Duhem equation can be used to check the consistency of the experimental data. When the excess Gibbs energy function is substituted into equation 3.45 together with equations 3.4 and 3.17, the Gibbs-Duhem equation at constant temperature and pressure is obtained

$$\sum x_i d \ln \gamma_i = 0 \quad (3.47)$$

The differential equation thus obtained can be applied to activity coefficients normalised by the symmetric or unsymmetric conventions, since the symmetric and unsymmetric conventions are used as boundary conditions in the integrated form of equation 3.47. A number of algebraic equations relating the activity coefficients to the liquid mole fractions can be obtained from equation 3.47. These algebraic equations satisfy equation 3.47 and typical examples are the Wilson, Van Laar and Margules equations.

The application and performance of these equations have been discussed in section 3.2.1 and the Wilson equation is used for the calculation of activity coefficients in this work.

Since the Gibbs-Duhem equation was derived assuming constant pressure and temperature, the activity

coefficients of the system will have to be calculated at the same constant temperature and pressure at which experimental data was determined. A rigorous thermodynamic relationship is given by equation 3.48 for the correlation of activity coefficients with respect to pressure between pressures p^1 and p^2 .

$$\gamma_i^1 = \gamma_i^2 \exp \int_{p^2}^{p^1} \frac{v_i^L}{RT} dp \quad (3.48)$$

The partial molar volume of the liquid i is denoted by v_i^L . The activity coefficient γ_i^1 has been modified for pressure and can be used in the Gibbs-Duhem equation.

3.3.6 Standard State Fugacity

Equation 3.49 is obtained when the activity coefficient is substituted from equation 3.48 into the liquid phase fugacity equation 3.17.

$$f_i^L = \gamma_i^2 X_i f_i^{OL} \exp \int_{p^2}^{p^1} \frac{v_i^L}{RT} dp \quad (3.49)$$

The normalisation conditions can now be applied to this equation for a pure liquid i at a reference pressure p^r and at the temperature of the solution. The result would be the standard state fugacity of the component i which is given by equation 3.50.

$$f_i^{OL} = p_i^s \phi_i^s \exp \int_{p_i^s}^{p^r} \frac{v_i^L}{RT} dp \quad (3.50)$$

The same procedure can be applied for the non-condensable system for which the standard state fugacity would be the Henry's constant for component i in a solvent

K at the temperature of the solution and at a reference pressure P^r .

$$f_i^{oL} = H_{i,r} P^r \quad (3.51)$$

Henry's constant can also be correlated for the effect of change in pressure by the following equation

$$H_i P^r = H_i^{P_k^s} \exp \int_{P^r}^{P_k^s} \frac{V_{i,k}^\infty}{RT} dP \quad (3.52)$$

Some simplifying assumptions can be used without introducing a large error to reduce the complexity of the above equations. The liquid molar volume was assumed not to change with pressure and the reference pressure was set to zero.

When these assumptions are applied to equation 3.50, the practical form of this equation for the system is given by

$$f_i^{oL} = P_i^s \phi_i^s \exp \left(-\frac{V_i^L P_i^s}{RT} \right) \quad (3.53)$$

The virial equation of state can be used to calculate the fugacity coefficient of component i at the saturation pressure.

$$\ln \phi_i^s = \frac{2}{V_i^s} B_{ii} - \ln Z_i^s \quad (3.54)$$

where

$$Z_i^s = \frac{P_i^s V_i^s}{RT} = 1 + \frac{B_{ii}}{V_i^s} \quad (3.55)$$

and V_i^s is the saturated molar volume of pure vapour i at system's temperature.

An alternative method for the calculation of ϕ_i^s has been provided by the three parameter corresponding states correlation of Lyckman, Eckert and Prausnitz (242). The fugacity coefficient of component i at the saturation pressure, ϕ_i^s , can be calculated at temperatures much closer to the critical temperature of component i than compared with equation 3.54

$$\log \phi_i^s = (\log \phi_i^s)_0 + \omega_i (\log \phi_i^s)_1 \quad (3.56)$$

where ω_i is the acentric factor and $(\log \phi_i^s)_0$ and $(\log \phi_i^s)_1$ are generalised functions of reduced temperature.

3.3.7 The Wilson Equation

The Wilson equation is probably the most widely used equation for correlating activity coefficients. The superiority of this equation over other equations has been noted by many researchers. Further advantages are that the equation is very flexible and a binary system is defined by a pair of constants, thus making the equation applicable for most systems. The Wilson equation can be used to correlate the activity coefficients for the formaldehyde systems. However, for other systems, different correlations may be more suitable depending on their physical nature.

For mixtures of molecules which are chemically

similar and differ only in size, a simple form of Gibbs energy function was derived by Flory and Huggins (243-4). According to the Flory-Huggins equation, ideal behaviour is expected whenever the components in the mixture have the same liquid molar volumes which are taken as a measure of the molecular size.

The case where the components in a mixture differ not only in molecular size but also in their inter-molecular forces was considered by Wilson (153) and later by Orye (159). Wilson's modification was based on the semi-theoretical arguments used by Flory and Huggins, which lacked the theoretical rigour of the lattice theory of Guggenheim (175).

For a binary system consisting of components 1 and 2 the probability of finding a molecule of type 2 relative to finding a molecule of type 1 about the central molecule of type 1 is expressed in terms of the overall mole fraction and two Boltzman factors.

$$\frac{X_{21}}{X_{11}} = \frac{X_2 \exp(-\lambda_{12}/RT)}{X_1 \exp(-\lambda_{11}/RT)} \quad (3.57)$$

The ratio of the number of molecules of type 2 to the number of molecules of type 1 about a central 1 molecule is expressed by equation 3.57 and is equal to the ratio of overall mole fractions of 2 and 1 weighted by the Boltzman factors. The parameters λ_{12} and λ_{11} are related to the potential energies of a 1-2 and 1-1 pair of

molecules respectively. The same procedure can be applied for the probability of finding a molecule of type 1 relative to finding a molecule of type 2 about a central molecule 2.

$$\frac{x_{12}}{x_{22}} = \frac{x_1 \exp(-\lambda_{12}/RT)}{x_2 \exp(-\lambda_{22}/RT)} \quad (3.58)$$

The local mole fractions can now be related by defining equations 3.57 and 3.58 in terms of fr_1

$$fr_1 = \frac{v_1^L x_{11}}{v_1^L x_{11} + v_2^L x_{21}} \quad (3.59)$$

where v_1^L and v_2^L are the molar liquid volumes of components 1 and 2.

Equations 3.57 and 3.58 can be substituted into equation 3.59.

$$fr_1 = \frac{v_1^L x_1 \exp(-\lambda_{11}/RT)}{v_1^L x_1 \exp(-\lambda_{11}/RT) + v_2^L x_2 \exp(-\lambda_{12}/RT)} \quad (3.60)$$

Similarly, the local volume fraction of component 2 is given by equation 3.61.

$$fr_2 = \frac{v_2^L x_2 \exp(-\lambda_{22}/RT)}{v_2^L x_2 \exp(-\lambda_{22}/RT) + v_1^L x_1 \exp(-\lambda_{12}/RT)} \quad (3.61)$$

The local volume fractions fr_1 and fr_2 were used by Wilson rather than the overall volume fractions used by Flory and Huggins. Therefore the molar excess Gibbs energy function of a binary system can be defined by

$$\frac{g^E}{RT} = X_1 \ln \frac{fr_1}{X_1} + X_2 \ln \frac{fr_2}{X_2} \quad (3.62)$$

To simplify the notation, two new parameters Λ_{12} and Λ_{21} are conveniently defined in terms of the molar volumes V_1^L and V_2^L and the energies λ_{11} , λ_{22} and λ_{12}

$$\Lambda_{12} = \frac{V_2^L}{V_1^L} \exp\left(-\frac{(\lambda_{12} - \lambda_{11})}{RT}\right) \quad (3.63)$$

$$\Lambda_{21} = \frac{V_1^L}{V_2^L} \exp\left(-\frac{(\lambda_{12} - \lambda_{22})}{RT}\right) \quad (3.64)$$

The Flory-Huggins equation as modified by Wilson then becomes

$$\frac{g^E}{RT} = -X_1 \ln(X_1 + \Lambda_{12}X_2) - X_2 \ln(X_2 + \Lambda_{21}X_1) \quad (3.65)$$

The excess Gibbs energy function is related to the activity coefficient by equation 3.66.

$$\left(\frac{\partial G^E}{\partial n_i}\right)_{T,P,n_j} = RT \ln \gamma_i \quad (3.66)$$

where

$$G^E = n_T g^E \quad (3.67)$$

and the total number of moles is defined by n_T .

When equation 3.65 is substituted into equation 3.66 the working equations for the calculation of activity coefficients is the result.

$$\ln \gamma_1 = - \ln(X_1 + \Lambda_{12} X_2) + X_2 \left[\frac{\Lambda_{12}}{X_1 + \Lambda_{12} X_2} - \frac{\Lambda_{21}}{X_2 + \Lambda_{21} X_1} \right] \quad (3.68)$$

$$\ln \gamma_2 = - \ln(X_2 + \Lambda_{21} X_1) + X_1 \left[\frac{\Lambda_{12}}{X_1 + \Lambda_{12} X_2} - \frac{\Lambda_{21}}{X_2 + \Lambda_{21} X_1} \right] \quad (3.69)$$

The general form of equations 3.68-69 for an m component system is represented by equation 3.70.

$$\ln \gamma_i = 1 - \ln \left[\sum_{j=1}^m X_j \Lambda_{ij} \right] - \sum_{k=1}^m \left[\frac{X_k \Lambda_{ki}}{\sum_{j=1}^m X_j \Lambda_{kj}} \right] \quad (3.70)$$

The two main features of the Wilson equation, parameters $\lambda_{12} - \lambda_{11}$ and $\lambda_{12} - \lambda_{22}$, may be assumed to be independent of temperature over a small temperature range. Thus the parameters obtained from data at one temperature may be used with reasonable confidence to predict activity coefficients at some other temperature close to the experimental temperature. This becomes an important advantage in isobaric distillation calculations where the temperature varies from plate to plate. A further advantage of Wilson's model is that a multicomponent system only requires parameters which can be obtained from binary mixtures. Thus the amount of experimental data required to characterise a multicomponent solution is thereby reduced.

The derived equations are seldom sufficiently precise



at temperatures near the critical temperature to justify their use when a non-condensable component exists in the system. A useful simplified version of the Wilson equation can be obtained by reducing it to the one parameter form. This assumption was used by Prausnitz et al (191) for a non-condensable component by setting Λ_{ji} equal to zero where i is the gaseous supercritical solute and j the solvent. This simplification, although arbitrary, can be practically justified since Λ_{ji} is much smaller than Λ_{ij} .

The one parameter form of the Wilson equation for the non-condensable component is defined by

$$\ln \gamma_i = \ln \left(\frac{\Lambda_{ir}}{\sum_{j=1}^m \Lambda_{ij} X_j} \right) - \frac{X_i}{\sum_{j=1}^m \Lambda_{ij} X_j} \quad (3.71)$$

where Λ_{ir} is the Wilson parameter for the non-condensable component in the chosen reference solvent r , which usually is the heaviest constituent of the system. However, any of the constituents of a multicomponent system can be chosen for the reference solvent depending on the accuracy of the available physical and chemical properties of the component.

The equation for determining the Wilson parameter for condensable-non-condensable interactions is slightly modified by using the partial molar volume at infinite dilution for the non-condensable component

$$\Lambda_{ij} = \frac{V_j^L}{V_{ij}} \exp \left[- \frac{(\lambda_{ij} - \lambda_{ii})}{RT} \right] \quad (3.72)$$

where j is the condensable component.

3.4 VAPOUR-LIQUID EQUILIBRIUM ACCOMPANIED WITH CHEMICAL REACTION

An accurate solution cannot be provided by the application of conventional vapour-liquid equilibrium calculation techniques to systems whose components react with each other. The values of the calculated thermodynamic and physical concepts such as activities, fugacities, partial pressures and vapour and liquid compositions would be altered by the presence of newly produced components from the chemical reaction. Therefore accurate results could not be provided by the conventional procedures unless the effect of the chemically produced components on the thermodynamic and physical concepts is thoroughly considered.

The conventional methods for calculating vapour-liquid equilibrium without considering the effect of chemical reaction were first applied to the formaldehyde-water system. The experimental data for the formaldehyde-water system were calculated from the algebraic relationships provided by Olsson and Svensson (73). The method and computer program to generate the experimental X , Y , P and T data are described in Appendix II.

Several optimisation techniques were employed to

estimate the binary interaction parameters of the formaldehyde-water system. The simplex, linear, Rosenbrock's gradient search methods of optimisation, were used to minimise the sum of the square of the errors between the calculated and experimental liquid phase mole fractions. The programs were written in BASIC language and were run on a Honeywell-316 computer.

The estimated parameters were then used to predict the vapour phase mole fractions for a given set of liquid phase mole fractions and pressure. It was found that the use of conventional vapour-liquid equilibrium techniques in which the components from the chemical reaction were not considered, were totally inadequate to relate the calculated and experimental results. However, some agreement between the calculated and experimental values was obtained for systems with a very low formaldehyde content. The effect of the chemical reaction would be reduced by the low formaldehyde content and thus the system would become similar to systems with no chemical reaction where conventional methods would accurately calculate the results.

Similar calculations were applied to the formaldehyde-water system, where the parameters were estimated using the normalised equations technique as suggested by Nagahama et al (221). However, no convergence was obtained. The equations and procedures for the phase equilibria

calculations, without considering the effect of chemical reaction, can be found in the earlier work on the formaldehyde systems (173).

For the ternary formaldehyde-methanol-water system, the data published by Walker (41) and Green and Vener (67) were used together with the same calculation procedures. Similarly, the effect of chemical reaction was ignored. No convergence was obtained, even though the more powerful technique of Marquardt was used.

Conventional phase equilibria calculation procedures had to be set aside because of the numerical instability and inability of the equations to provide good vapour-liquid equilibrium results. Therefore, the method of calculation had to be modified to include the effect of chemical reaction.

The reactions of formaldehyde with water and methanol in the vapour and liquid phases have been discussed previously in chapter 2. The resulting constituents of the formaldehyde-water system are formaldehyde, methylene glycol and water which are in chemical equilibrium with one another. Although other chemical reactions may occur in the formaldehyde-water system, such as the polymerisation of formaldehyde, the hydration of formaldehyde to methylene glycol has been considered as the most significant reaction in the system. In a freshly made formaldehyde-water solution, a long time is needed for

the polymerisation reactions to be completed and the resultant polymers have a low concentration. Thus the results from the phase and chemical equilibria are not seriously altered by ignoring the effect of the reaction of formaldehyde with water giving the various polymers.

The ternary formaldehyde-methanol-water system can be considered as a mixture of formaldehyde-hemiformal-methanol-methylene glycol-water. The hemiformal is formed as the first product from a series of reactions between formaldehyde and methanol. Therefore similar reasoning can be applied for neglecting the reactions leading to the heavier polymers resulting from the reaction of formaldehyde with methanol.

The reaction rate constants for the chemical reactions of formaldehyde with water and methanol are assumed only to be a function of temperature. The equilibrium constants can be presented in the general form of

$$\log K = A + \frac{B}{T} \quad (3.73)$$

where the parameters A and B specify the chemical equilibrium constant according to the different reactions. Since the reactions occur both in the liquid and vapour phases, the equilibrium constants need to be specified for each phase for the same reaction. Thus for each reaction, the equilibrium constants for the two phases are defined by four parameters. The numerical values and calculation procedures for these parameters are

presented in detail in Appendix III.

3.4.1 Formaldehyde-Water System

In the binary formaldehyde water system, methylene glycol is formed as a result of the hydration of formaldehyde. Because of this reaction, formaldehyde only method exists in a very low concentration as a free component in the solution and methylene glycol must now be considered as one of the major components in the system. There is a large difference between the physical properties of formaldehyde and methylene glycol (for example the boiling point difference at atmospheric pressure is about 200°C). Therefore, it would be an error to omit methylene glycol as one of the components in the system, especially as in a binary solution, formaldehyde and water cannot be prepared without having any methylene glycol in the system.

The chemical reaction equilibrium relationships as well as the phase equilibria equations must be satisfied by the concentration of the reacting systems. An extra constraint is imposed on the composition of an associating system by the difference between the phase equilibria calculations for the associating and non-associating systems. The resulting ternary formaldehyde-methylene glycol water system can now be analysed so that the phase equilibria and chemical equilibrium relationships can be applied simultaneously. As the chemical equilibrium occurs in both the vapour and liquid phases, the reactions

in the two phases must be included in the calculations.

Many mathematical models have been proposed for the phase equilibria of reacting systems. Care must be taken in selecting a model for such systems as the requirement of the physical or experimental data varies from one method to another. The ternary formaldehyde-methylene glycol water system can be composed of three binary systems.

- (1) Formaldehyde-methylene glycol.
- (2) Formaldehyde-water
- (3) Methylene glycol-water.

No method has yet been devised to prepare anyone of these binary solutions free from the third component, because the components in the appropriate binary would simply react to produce the third component. Because methylene glycol has not been isolated, almost no physical data has been reported for this component. Furthermore, the physical data reported for formaldehyde have been found to be unreliable. Therefore the necessary data such as the critical temperature, pressure and volume have to be estimated using different generalised techniques. The vapour pressures of these components also have to be estimated or be calculated by making simplifying assumptions.

Each of the hypothetical binary systems composing the ternary formaldehyde, methylene glycol and water system, will have to be specified by the appropriate parameters. The free formaldehyde has been considered as a non-

condensable component, having a very low boiling point and critical temperature. The critical temperature of formaldehyde has been reported as being not much higher than the boiling point of the ternary mixture. Therefore each binary involving free formaldehyde will be specified with Henry's constant and the Wilson equation single parameter. The condensable binaries will be specified with the Wilson equation binary interaction parameters for the calculation of the activity coefficients. The available physical property data and the data which had to be estimated are represented in appendix IV and V.

The model for the phase and chemical equilibria was initially based on distinguishing between the original compositions expressed as mole fractions and the compositions after the chemical reaction has reached the equilibrium stage. The chemical reaction can be represented by the following equation



The original mole fractions are denoted as the stoichiometric mole fractions and the mole fractions at chemical equilibrium are denoted as the true mole fractions. Thus the true and stoichiometric mole fractions can be related by a mathematical relationship in terms of the chemical equilibrium constants. If the higher hydrates of formaldehyde are neglected, formaldehyde is present in two different chemical forms, namely free formaldehyde and

methylene glycol, in a formalin solution. At chemical equilibrium the true mole fractions can be related to the number of moles of each component by equations 3.75 and 3.76.

$$x_i = \left(\frac{n_i}{\sum_i n_i} \right) L \quad (3.75)$$

$$y_i = \left(\frac{n_i}{\sum_i n_i} \right) V \quad (3.76)$$

where i = formaldehyde, methylene glycol and water and n_i is the number of moles of component i .

A model has been developed for the phase equilibria, considering the chemical reactions. The binary parameters can be estimated through calculation procedure based on this model. In order to estimate parameters for any binary solution, the system will have to be specified by sets of experimental data consisting of vapour and liquid compositions, pressure and temperature.

Because the binary systems composing the ternary formaldehyde-methylene glycol-water systems do not physically exist, the parameters were estimated simultaneously for all the binary systems.

The estimation of parameters was based on minimising the square of the difference between the calculated and experimental pressure because the total pressure of the

system is a singular concept which is related to all of the estimated vapour phase compositions.

$$S = \sum_{i=1}^M (P_{EXP,i} - P_{CAL,i})^2 \quad (3.77)$$

where

$$P_{CAL,j} = \sum_{j=1}^m P_{CAL,j} \quad (3.78)$$

and M is the number of data points and m is the number of components. The advantage of this method is that the calculated vapour phase compositions can be compared with the experimental values to confirm the validity of the estimated parameters.

The calculation procedure can be summarised as follows:

- (1) Calculate the true liquid phase mole fractions which are in chemical equilibrium at the system's temperature.
- (2) Estimate the initial guess for the parameters.
- (3) Calculate the thermodynamic properties.
- (4) Evaluate the intermediate vapour phase mole fractions.
- (5) Modify the intermediate vapour phase mole fractions according to the vapour phase chemical equilibrium relationships.
- (6) Calculate the partial pressure of each component.
- (7) Find the total pressure of the system.

- (8) Evaluate the sum of the square of the errors.
- (9) Check the sum of the square of the errors with the preset tolerance limit.
- (10) If the sum of the square of the errors is greater than the preset tolerance, update parameters and repeat the calculations from step 3.

The calculations were stopped when the required accuracy was reached in step 9 and the current estimated parameters were taken as the solution for this correlation.

The equations relating the true and stoichiometric mole fractions for both the liquid and vapour phases can be found in Appendix I.

The experimental vapour and liquid mole fractions, pressure and temperature data used in this method were generated by the procedure presented by Olsson and Svensson (73). The equations for this procedure can be found in Appendix II.

3.4.2 Formaldehyde-Methanol-Water System

The mixture of formaldehyde, methanol and water is the common form of commercial formaldehyde solution. Small quantities of methanol are retained in the solution to inhibit the polymerisation and subsequent precipitation of formaldehyde. Due to the presence of an extra component, extra binary sub-systems have to be added to the existing binary systems which were correlated in

Section 3.4.1. The resulting hypothetical binary systems, neglecting the reaction product of formaldehyde with methanol, can be classified as follows:

- (1) Formaldehyde-methanol
- (2) Formaldehyde-methylene glycol
- (3) Formaldehyde-water
- (4) Methanol-methylene glycol
- (5) Methanol-water
- (6) Methylene glycol-water

Methanol-water is a real system and the parameters describing this system have been well-documented (191). The parameters for binary systems 2, 3 and 6 have been estimated by the procedure outlined in Section 3.4.1.

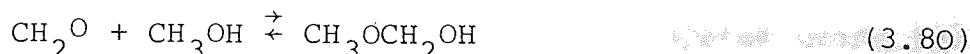
The interaction parameters for the new binary systems 1 and 4 must now be calculated in order to characterise the formaldehyde-methanol-water system.

The parameters can be estimated by the same technique which was used for the formaldehyde-water system. The experimental data of Walker (41) and Green and Vener (67) were used to estimate the interaction parameters. However the system was poorly correlated using the binary interaction parameters for the six binary systems. Therefore, it became evident that the reaction of formaldehyde with methanol must be considered in the modelling of the system.

Hemiformal is produced as the first product of the reaction of formaldehyde with methanol: hemiformal has

not been isolated and is an unstable component only in equilibrium with formaldehyde and methanol. Hemiformal cannot be isolated due to the instability of the molecule: the heavier reaction products of formaldehyde with methanol are more stable and can be isolated. The effect of the heavier products is assumed to be negligible since the long reaction time required and the low concentration of these products will reduce their effect to a minimum. Furthermore, traces of these heavier and more stable components were not observed in the analysis of samples containing methanol.

Thus the two significant simultaneous chemical reactions occurring in formaldehyde-methanol-water system would be:



The chemical reactions and the phase equilibrium are illustrated in Figure 3.1.

The hypothetical and real binary systems resulting from the quinary formaldehyde-hemiformal-methanol-methylene glycol-water system can be tabulated:

- (1) Formaldehyde-hemiformal
- (2) Formaldehyde-methanol
- (3) Formaldehyde-methylene glycol
- (4) Formaldehyde-water

- (5) Hemiformal-methanol
- (6) Hemiformal-methylene glycol
- (7) Hemiformal-water
- (8) Methanol-methylene glycol
- (9) Methanol-water
- (10) Methylene glycol-water

From the ten binary systems only methanol-water is a real system and the remaining nine were considered to be hypothetical systems. The interaction parameters and Henry's constant for systems 3, 4 and 10 have been estimated in Section 3.4.1. The binary interaction parameters and Henry's constants for the binary systems 1, 2, 5, 6, 7 and 8 had to be estimated.

The parameters for these binary systems were estimated simultaneously employing the procedure used for correlating the formaldehyde-water system. The experimental X, Y, P and T data were calculated for the quinary system using the stoichiometric mole fractions and reaction constants for the vapour and liquid phases. The equations for these calculations are described in Appendix I.

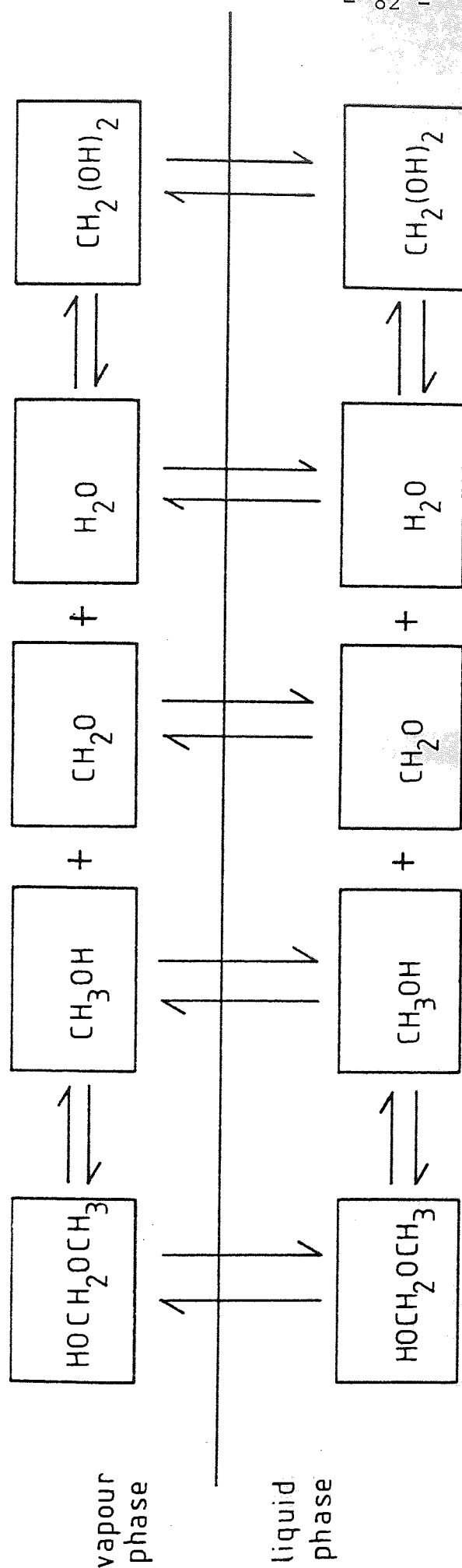


Figure 3.1 Chemical and phase equilibrium of formaldehyde, methanol and water solutions

CHAPTER 4

MATHEMATICAL MODEL OF DISTILLATION COLUMN

4. MATHEMATICAL MODEL OF DISTILLATION COLUMN

4.1 INTRODUCTION

Before the application of computing methods to distillation problems, rigorous methods for the calculation of distillation columns were more of hypothetical interest rather than practical interest. Short-cut methods were used by distillation column designers instead of attempting the lengthy calculations required by the rigorous procedures. However, when computers came into general use, interest was revived in the use of these procedures. They had been originally conceived for manual calculations and therefore the methods had to be modified for application to computers. However, some problems were caused by the computer calculations, usually in the form of numerical instability and the modelling of the distillation system.

The first stage in the design of a distillation column is to determine the heating and cooling requirements, the number of plates in the column and the location of the necessary feeds and side streams to achieve the specified separation. No design procedure has been published which will permit the solution of this problem with a precision limited only by the extent and accuracy of the data available despite the large amount of literature published on this subject area.

4.2 LITERATURE SURVEY

Distillation in the period of 1921 to 1932 has been

reviewed by Keyes (84), the period of 1941 to 1954 was surveyed by Rose (85) and some of the patents granted between 1955 and 1960 were listed by Mamers (86). The recent advances in distillation between 1962 and 1971 were reviewed by Bolles and Fair (87). A review on distillation was published by Holdsworth (88), in 1963 whilst the aspect of distillation with chemical reaction was covered up until 1971 by Davies (89).

A large amount and variety of literature apertaining to distillation is still published each year and it would not be possible to cover every detail or aspect of distillation, therefore only modelling and the performance of models will be discussed.

Generally all the modelling techniques and methods for steady-state distillation can be categorised into four main sections (93).

1. Stage to stage methods, e.g. Lewis and Matheson (90).
2. Generalised matrix methods, e.g. Wang and Henke (91).
3. Linearised simultaneous solution approach, e.g. Naphtali and Sandholm (92).
4. Miscellaneous methods.

4.2.1 Stage to Stage Methods

The plate to plate calculation technique was introduced

by Sorel (94) in 1893 and most methods have been built on this technique. A method for multicomponent mixtures was first developed by Lewis and Matheson (90).

The product compositions consistent with the specification and the overall balance are first estimated. Then essentially, Sorel's (94) plate to plate procedure is used inward from each end of the column assuming constant reflux ratio rates. Finally the product distributions resulting from the mismatch of the compositions at the feed plate are re-estimated.

A plate to plate calculation procedure was proposed by Thiele and Geddes (95) which avoids the estimation of the product compositions by replacing this with the estimation of the equilibrium ratios for all the plates. In this method only ideal mixtures were considered, thus reducing the problem of estimating the temperature profile of the column. A group of equations were suggested by Murdoch (96) for the solution of the distillation column. The mass and energy balance equations in conjunction with the phase equilibria relationships were generalised and solved by a plate to plate procedure. In the method proposed by Bonner (97), the number of plates required for a given reflux rate and separation, together with the feed plate position chosen to minimise the total number of plates in the column, were determined. The position of the optimum

feed plate was proposed by Gilliland (98). The basic Thiele and Geddes (85) method was extensively developed by Holland et al (99) and the rate of convergence was improved by using the theta method for correcting the product distribution. The difference and performance of the Lewis and Matheson (90) and Thiele and Geddes (95) methods have been described by Sargent and Murtagh (100). The studies made by McIntire and Shelton (101), Holland and Lyster (102) and Hanson and Duffin (103), were all based on the plate to plate calculation technique. A stagewise calculation based on the Thiele and Geddes (95) method was used by Lyster et al (104) where the equations were modified to include the calculation of an unlimited number of side streams: the plates were assumed to be equilibrium stages and the Newton-Raphson method was used to solve the resulting nonlinear equations. A modified Newton-Raphson method was used by Greenstadt, Brad and Morse (105) for the solution of the distillation column equations by a tray to tray method. At particular locations called mesh points, certain conditions were checked. The calculations were repeated if the set conditions were not met.

4.2.2 Generalised Matrix Methods

An iterative method was developed by Wang and Henke (91) for the solution of complex multicomponent

distillation columns. Each stage was assumed to be an equilibrium stage in which the liquid and vapour phases leaving any plate were in equilibrium. This model is based on four sets of generalised equations for each stage; mass balance, energy balance, equilibrium and summation equations. The mass balance and equilibrium equations are combined together and substituted for the liquid or vapour flow rates in a general form. These equations can then be defined in terms of the liquid phase mole fractions for three consecutive equilibrium stages for any component. The general equations then can be written in a matrix form. A tridiagonal matrix can be obtained and the matrix coefficients can be calculated for any position according to their general expressions. An initial temperature profile and vapour flow is assumed and the flow rates and compositions of the feed and product streams are specified. The coefficients of the tridiagonal matrix then can be calculated provided that the equilibrium ratios are only a function of temperature. The solution of the tridiagonal matrix provides a new set of liquid mole fractions. The solution of equilibrium equations then provides a new temperature profile which is used to calculate new values for the vapour flow rates. This procedure is then repeated until convergence is achieved.

Wang and Henke claimed that the solution of large matrices which would be needed in other modelling techniques is avoided, thus reducing the computation time and storage needed. A better convergence and numerical stability is also achieved.

The method developed by Wang and Henke (106) is based on the method described by Amundson and Pontinen (107). The mass and energy balance equations are combined with the equilibrium relationships, set in matrix form. As the matrix equations are grouped by tray numbers the resulting matrix is tridiagonal. The energy balance equations are also set in another matrix. The vapour flow rates in the column are given by the solution of this matrix. The Newton-Raphson approximation method was used in order to solve the equilibrium equations. The technique was improved by Amundson, Pontinen and Tierney (108) by including the calculation of a complete heat balance, inert injection and internal reflux cooling. The approach of Amundson and Pontinen (107) was further improved by Sargent and Murtagh (100) with additional refinements to eliminate convergence problems and to extend the equations for the solution of real plates.

A modification to the tridiagonal matrix method was proposed by Jedlovszky (129) by the linearisation of the

matrix coefficients. A faster and numerically more stable solution was claimed by the author.

4.2.3 Linearised Simultaneous Solution

A procedure was proposed in 1967 by Stainthorpe and Whitehouse (109) which consisted of solving the material and energy balance equations, as nonlinear simultaneous equations. This approach has been further refined by Naphtali and Sandholm (92) and Goldstein and Stanfield (110).

The mass and energy balance, equilibria and summation equations were used by Naphtali and Sandholm (92) to model the distillation column. The equilibrium equations were combined with the Murphree plate efficiency expression. Therefore each plate was represented by three sets of equations which were solved simultaneously. A modified Newton-Raphson procedure was used to linearise and solve the resulting equations. The final matrix was in the form of a tridiagonal matrix for which each coefficient of this matrix was a matrix on its own. The A matrix or the first coefficient of the tridiagonal matrix was defined as the derivative matrix of functions of plate i with respect to the variables on plate $i-1$, the B matrix or the second coefficient of the tridiagonal matrix was defined as the derivatives of the functions of plate i with respect to the variables of plate i , and

the c matrix or the third coefficient of tridiagonal matrix was defined as the derivatives of the functions of plate i with respect to the variables of the plate i+1.

The correction term was provided by the solution of this matrix for all the variables in the column and a new set of variables was calculated which in turn updated the overall tridiagonal matrix. The solution was reached when the correction terms of all the variables were less than the predetermined accuracy limit. It is claimed by Naphtali and Sandholm (92) that the component volatility range does not affect the convergence, the presence of nonideal solutions is accounted for in the model, specifications can be set in the program as desired, the Murphree efficiency is taken into account and an unlimited number of side streams can be accommodated. As the solution is approached, the rate of convergence is accelerated and no difficulties are caused by small values generated in the program. For the solution of a 100 plate distillation column with 20 components, a storage capacity of 98600 words on the computer is required and this large storage requirement is a major disadvantage.

A similar technique of construction for the overall matrix has been used by Goldstein and Standfield (110) but the equations are grouped by component rather than by plate location and therefore the final matrix is not

tridiagonal. Because of the very large size of the matrix, the solution of this matrix is carried out by partial triangularisation.

Tierney and Bruno (111) stored the equations in a matrix form and by employing a number of assumptions the resulting matrix was simplified and solved by the Newton-Raphson method.

4.2.4 Miscellaneous Methods

The relaxation method was used by Rose, Sweeny and Schrodtt (112) for calculating the product compositions in a multicomponent distillation column using a plate to plate technique, when all the design parameters were established. In the relaxation method, calculations are made by a gradual change in all the plate and product compositions that occur in a column from an initial start up value until steady state is reached. This approach was thought to reflect the physical stability of the column on the convergence of equations describing the system. However, the numerical difficulties associated with the integration of the relevant differential equations are still present, as described by Mah, Michaelson and Sargent (113) and by Pollard (114).

A more stable integration method was used by Rosenbrock, Tavendale, Storey and Challis (115). A satisfactory

estimate of the steady state was observed. Examples are also given by Ball (116) but slow convergence was achieved. A modification of the method described by Holland (99) has been presented by Billingsley (117) and this modification exhibits a substantially improved convergence characteristic. The relaxation method was used by Jelinek, Hlavacek and Kubicek (118) for the solution of multicomponent separation processes. This method can be applied to multiple feed distillation columns with nonideal solutions. The modification applied to the relaxation technique by Jelinek, Hlavacek and Kubicek resulted in a pentadiagonal matrix. Multicomponent separation processes for the solution of a nonlinear boundary value problem for a set of difference equations have been analysed by Kubicek, Hlavacek and Jelinek (119). The procedure is based on some initial guessed value for one of the parameters of the column. The solution of the equations of the column had to predict a new value for the initially guessed parameter until a desired accuracy has been reached. The successive solution of design equations by simultaneous correction type solution, in which the column configuration is adjusted and iterated until a solution has been reached, was described by Ricker and Grens (120).

The application of mathematical techniques such as perturbation has been used by some workers in the modelling

of distillation columns because of the stagewise nature of the equations involved. The calculation technique developed by Acrivos and Amundson (122, 123), based on the perturbation technique for nonideal solutions has been modified by Hirose, Hiraiwa and Sudoh (121). The method proposed by Saita and Sugie (124) is a modified successive iteration method for the plate to plate calculation of distillation columns by the perturbation method. This method was applied to a nonideal multicomponent distillation system with one feed.

4.2.5 Distillation with Chemical Reaction

A limited number of papers have been published on the subject of modelling distillation with chemical reaction. Generally, the method of the solution of the design equation is not seriously affected by the inclusion of a chemical reaction in the distillation process, although the equations have to be modified to include the effect of the chemical reaction.

A method for the calculation of distillation with chemical reaction was reported in 1955 by Belck (125). The method was proposed for hypothetical two and three component liquid-phase reversible reactions. A continuous process is described in which the products are obtained in essentially pure form by carrying out the reaction in a single distillation column. A plate to plate calculation

technique was employed for this purpose and this type of calculation has been reported in detail by Mamers (86) and Davies (89). A method of calculation for batch distillation with chemical reaction has been published by Nishi (126). The differential equations which represent the variation of the composition of a component in the column as a function of time were solved simultaneously and numerically. With a minor modification of this calculating method these equations can be applied to continuous distillation. The significance of the heat of reaction is also included in the equations. For continuous distillation, the dynamic solution is also obtained from start up until steady state is reached. The application of an iterative method for the determination of stage temperature, stage reaction rate and inter-stage flow rates in the problem of multicomponent distillation accompanied by a simultaneous chemical reaction has been described by Suzuki et al. (127). A modified Muller's method (106) was applied for the convergence of the column temperature profile. Muller's method (106) has also been used in most of the methods and techniques mentioned previously. The derivation of the equation is simplified by using matrix notations. For the solution of the linearised material balance equations the tridiagonal matrix algorithm was employed. A similar technique of calculation has been employed by Baratella, Carra and

Santi (128).

The formulation of a solution method for the equilibrium-stage mode equations and the decisions are involved in grouping and formulating the design equations were discussed by Friday and Smith (130). The problem of convergence was also discussed and a method of solution for the concentration or component rate matrix was, however, introduced.

4.2.6 Plate Efficiency

Efficiency is referred to as the ratio of the number of theoretical plates to the number of actual plates in a distillation column required for a given separation. Thus the variation in performance of an actual distillation plate in a column from that of an ideal plate is shown by the value of the efficiency.

Efficiency in distillation has been extensively studied with the result that many papers have been published. The numerical evaluation of efficiency is generally carried out by the use of either simplified empirical correlations or the application of more theoretically based relationships.

The simple empirical methods of Drickamer and Bradford (131) and O'Connell (132) have been developed to predict tray efficiency as a function of the liquid viscosity and component relative volatility. The basic

mass-transfer approach is ignored and therefore the methods are simple to use. However, as the correlations are empirical, only those systems upon which they are based are adequately represented, and therefore their use for other systems may be doubtful. Also only one or two of the many variables involved are utilised in these methods and a complex problem is over simplified. However, an estimate of the efficiency can quickly be obtained from these correlations.

The most reliable method for prediction of efficiency data is to use existing experimental data, but the use of such a method is restricted to the very well defined and known systems for which such data are reported. The two previously mentioned methods cannot be applied to many systems because of the lack of experimental data or the complexity of the system. In such systems where there is no other alternative, the efficiency factor would have to be calculated from theoretical based relationships. These methods are generally based on the method developed by the A.I.Ch.E. tray efficiency research program (133). In this method the efficiency is assumed to be a function of four main factors - the rate of mass transfer in the vapour phase, the rate of mass transfer in the liquid phase, the degree of liquid mixing on the tray and the amount of liquid entrainment between the trays. A precise prediction of efficiency requires that each of these

factors can be properly evaluated and taken into account.

Separate correlations for each of these factors and the way the correlations can be used to predict the efficiency are given in the A.I.Ch.E manual. The major steps in the prediction method are (a) the prediction of point Murphree efficiency (134) from the mass transfer characteristics of the vapour and liquid, (b) the assumption of some liquid mixing model on the tray in order to relate the point efficiency to the Murphree tray efficiency, (c) the correction of the Murphree tray efficiency for entrainment and (d) the calculation of the overall column efficiency from the corrected Murphree tray efficiency.

Many articles have been published each giving a new correlation for the previously mentioned sections. Many of these articles can be found in the International Symposium on Distillation (135, 136) and Institution of Chemical Engineers Meeting on Distillation (93). (133).

Ludwig (137) has stated that the method of A.I.Ch.E., although somewhat untried at that time in all fields, was believed to produce reliable results. The much earlier work of O'Connell (132) is reported (138) to give results much lower than those of the A.I.Ch.E. method (133). However, Ludwig reported that O'Connell's method gives good result for hydrocarbon mixtures.

although the values obtained would be high. It has been suggested in the Glitch design manual (139) that the values based on O'Connell^{'s} method were approximately correct whilst it was reported in the Hydronyl manual (140) that the results from the A.I.Ch.E. manual were correct. Recently a computer program has been developed to calculate the tray efficiencies using the A.I.Ch.E. method (138).

All the mentioned methods have been developed for binary systems for which the efficiency is equal for both components. However, in multicomponent systems, each component efficiency can be different and may become greater than unity or take negative values. The prediction of tray efficiencies for binary systems is well documented, whilst very few investigations of tray efficiency in ternary or multicomponent systems have been reported. (141-4). However, it is claimed that the A.I.Ch.E. method can be applied to a multicomponent system (133). The accuracy of the results obtained for components whose efficiency is negative or greater than one, must be in doubt.

The amount of information available for the efficiency of systems where a chemical reaction occurs in the distillation column has been found to be sparse. The majority of such systems involving a chemical reaction are

multicomponent systems and thus the complexity of the problem is increased. The performance of a distillation column in which a chemical reaction is being carried out has been analysed by Mamers (86) and Davies (89) in terms of plate efficiencies. They both concluded that the effect of chemical reaction would be best demonstrated by the Murphree plate efficiency and subsequently positive, zero and negative values were calculated.

The most related work on the efficiency of the formaldehyde system was recently reported by Olsson and Svensson (73). Their model for formaldehyde-water mixture is based on the A.I.Ch.E. method with some modifications. However, in estimating the efficiencies of this system, the effect of the reaction product, methylene glycol, was ignored, thereby reducing a ternary system to a binary.

4.3 DISTILLATION CALCULATIONS

Identification of all the vapour, liquid and feed streams can be used as a helpful starting point for modelling a distillation column. However, at this stage the number of plates or the location of feed plate may or may not be known.

A unique set of stream rates, composition, temperature and pressure will be produced by the specification of a relatively small number of variables in a distillation column. The purpose of any rigorous calculation method is

the prediction of the unique set of conditions which will exist in the operating column under any desired set of specified variables. Values of some of the unspecified variables usually have to be assumed in order to start the calculations which will renew the estimated values of these variables. The calculated values are then compared with the assumed values in a trial and error procedure.

The total number of variables in a distillation process can be divided into three groups.

1. Specified variables
2. Assumed iteration variables
3. All other iteration variables

The specified variables are those which are defined to establish a unique operation of the process. The necessary number of specified variables for any process can be determined by the basic information on a system. These variables remain constant throughout the whole calculation of any given problem.

The assumed iteration variables are those which are assigned a value at the beginning of the calculations in order to start the trial and error procedure. The values of iteration variables are changed for each iteration.

The values of these variables which are calculated

in each trial are then used for the new estimate in the next iteration.

All the other iteration variables are then defined as those parameters which are not defined in the groups 1 and 2. The final values of the variables in groups 2 and 3 are fixed once the solution has been reached. Generally, the calculation procedure for multistage separation processes can be divided into certain basic steps.

1. The specification of the process. This is accomplished by listing a sufficient number of specified variables.
2. The preliminary assumptions. The initial values for the assumed iteration variables are provided by these assumptions and they must be guessed to start the trial and error procedure. Temperature, liquid and vapour flow rate profiles throughout the column are among these variables.
3. The calculation procedure. This step is governed by the strategy chosen for the calculations.
4. The method chosen to accelerate the convergence of the solution. This is controlled by the method of calculation and the available information.
5. The calculation of new estimates for the initially guessed values.

6. A convergence check. A decision is taken whether to stop or repeat the calculations.

The next important decision in the modelling of a distillation system is the selection of the method of solution. The short-cut methods which over simplify the problem and give a rapid estimate for the problem, cannot usually be applied to complex systems and thus are not suitable for formaldehyde solutions. The rigorous methods of solution for the static distillation problem can be categorised into two sections namely the simultaneous solution of the stage equations and the stage to stage method of solution. These methods and their various types have been discussed earlier in Section 4.2.1.

For most methods, the mass and energy balance equations are combined with the phase equilibria equations and the iterative solution of the phase equilibria equations forms a part of the overall iterative solution of the distillation column. In this work the phase equilibria equations and their solutions have been developed independently from the column equations. In order to reduce the complexity of the final working equations for the solution of the distillation column, the phase equilibria part of the model was separated from the iterative solution of distillation column. Using this procedure the iterative solution of the phase equilibria does not interfere with

the iterative solution of distillation column. However the two iterations are inter-related because the input information to any of the sections, phase equilibria or column equations, is the result of the calculation in the other section. This can be explained further by considering the iterative solution of the phase equilibria section for temperature and vapour phase composition with a given set of liquid phase compositions and pressure. The calculated temperature and vapour phase mole fractions are utilised in turn by the column calculating section to provide a new set of liquid phase mole fractions. The calculations are iterated between the two sections until the solution is reached.

The exchange of information between the two sections is not altered by the simultaneous or stage to stage method of calculation as the liquid mole fractions are calculated simultaneously in the first method and individually in the second method. The calculated values of the liquid mole fractions are then introduced as the input information for the phase equilibria section.

The use of simultaneous solution methods has been encouraged by the rapid development of modern computers with very large storage capacity, as these methods require a large memory core in the computer to store the large matrices. The numerical stability and ease of application to complex distillation systems has been claimed as a

major advantage of this method.

One of the most important methods of simultaneous solution is the tridiagonal matrix method. A modified version of the tridiagonal matrix method was applied to the distillation of formaldehyde, water and methanol solutions. However satisfactory results were not obtained from this method as the numerical instability in the calculations prevented the convergence of the solution.

The tray to tray method of calculation was used as an alternative calculation method. The methods and equations for both of the techniques are discussed in detail in Sections 4.3.1 - 2.

Each stage is represented by the equations based on the mass and energy balance combined with the relationships for the chemical reaction, resulting in a set of equations. The strategy for the solution of these equations is decided by the application of ^{the} method of solution.

4.3.1 Tridiagonal Matrix Method

The objective of developing a model for the system of formaldehyde-methanol-water is to obtain a method by which the formaldehyde system can be designed or evaluated. The resulting model represents the steady state simulation of the distillation of formalin solutions. The performance and accuracy of the model can be ascertained from the

comparison of the calculated and experimental results.

The assumptions and the given factors involved in the calculations must first be specified. A schematic diagram of the system can be useful in clarifying the flows and stages. Then the mass and energy balance equations can be set up for the system. The equations are rearranged in a suitable form to be used in the matrix form. The equations are solved by the tridiagonal matrix method using a computer program developed for this purpose together with the computer programs for the phase equilibria.

Since an existing distillation column is to be modelled, a number of parameters can be specified in order to create similar conditions in the model based on the parameters and operating variables in the actual distillation column. Some of the parameters are fixed by the actual design of the distillation column such as the number of trays, type of trays, free area of the trays, condensation condition and limitations of the distillation column. These parameters are the characteristics of the distillation column and their values are not changed during the experiments. The operating parameters are the heat input to the boiler, vapour and liquid flows on the plate, cooling water rate in the condenser, heat input to the feed heater, feed temperature, feed plate position, feed flow rate, composition of the feed, reflux ratio, liquid holdups of the trays and the distillation regime. These variables can be controlled

and varied in different experiments. There are a number of parameters which could not be controlled thoroughly such as the distillation pressure and temperature of the laboratory. When the above mentioned variables were fixed a unique set of results such as temperature profile, composition profile, flow rates of top and bottom products and their composition can be obtained from both the experimental data and the mathematical model and thus a comparison can be made between the experimental and calculated results.

The distillation column used in this work is described fully in Chapter 6. Essentially it was designed to have eight sieve plates, 76 mm diameter with a total condenser and variable reflux ratio. The tray liquid hold up, feed tray position, feedrate and heat input to the boiler and feed heater could also be varied.

The chemical reactions which can occur in the column namely the hydration of formaldehyde and the reaction of formaldehyde with methanol, have been described in Chapters 2 and 3. The insignificance of the reactions leading to heavier polymers becomes evident especially when the relatively short residence time of the vapour and liquid phases, combined with the high temperatures in the column are considered. Although the average residence time of vapour and liquid streams may be small it is assumed that

the reactions leading to methylene glycol and hemiformal are completed on each tray. This assumption is made on the basis of the very fast rate of the two reactions. A study of the available data on the rate of the two reactions has shown that the reactions reach equilibrium in a fraction of a second. However, insufficient data are available on the rates of the reaction for hydration of formaldehyde and the reaction of formaldehyde with methanol. The lack of data on the rates of the reaction is probably caused by the uncertainties in the kinetics of these reactions.

It has also been assumed that the pressure drop on each plate is negligible since the liquid height on each plate is comparatively small. The actual pressure drop across the column was found to be approximately 3 kNm^{-2} and was therefore considered to be negligible.

The escape of a small quantity of free formaldehyde from the top of the column has been considered to be negligible since the concentration of free formaldehyde in the vapour entering the condenser is the lowest in the column. Free formaldehyde is reduced further by the condensation process because the free formaldehyde is converted to less volatile components.

4.3.1.1 Plate Model

A schematic diagram of the column is shown in figure 4.1 consisting of ten stages numbering the stages from the reboiler as stage one to the condenser as stage ten. Each stage is thus numbered from the bottom to the top. The general layout of the stages is shown in figure 4.2. Each stage as shown in figure 4.3 is assumed to be the combination of three sections. There is a mass-transfer section where the entering vapour and liquid phases are contacted with each other and mass transfer occurs between the phases. There are two reaction sections, one for the leaving vapour and one for the effluent liquid. The components in the streams come to a new chemical equilibria as the existing chemical equilibria in the entering streams were disturbed by the transfer of components from one phase to another in the mass transfer section.

The mass transfer section can be considered to be similar to an ordinary distillation column plate for a non-reacting system. The vapour and liquid reaction stages can be taken to be analogous to a gas phase and a liquid phase reactor respectively.

The following model has been obtained when the approach used in the tridiagonal method has been combined with the phase equilibrium model. However, no results

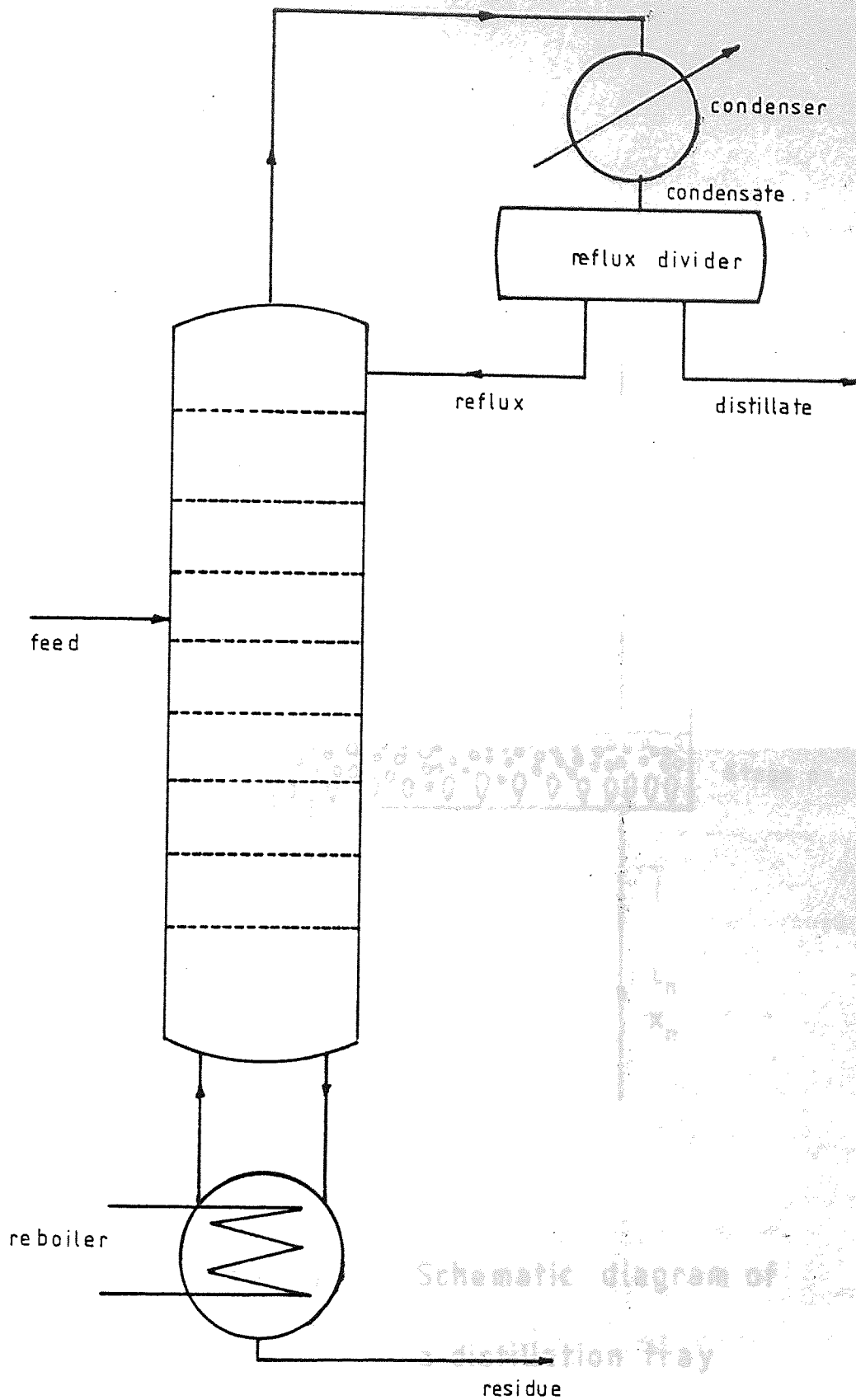


Figure 4.1 Schematic diagram of distillation column

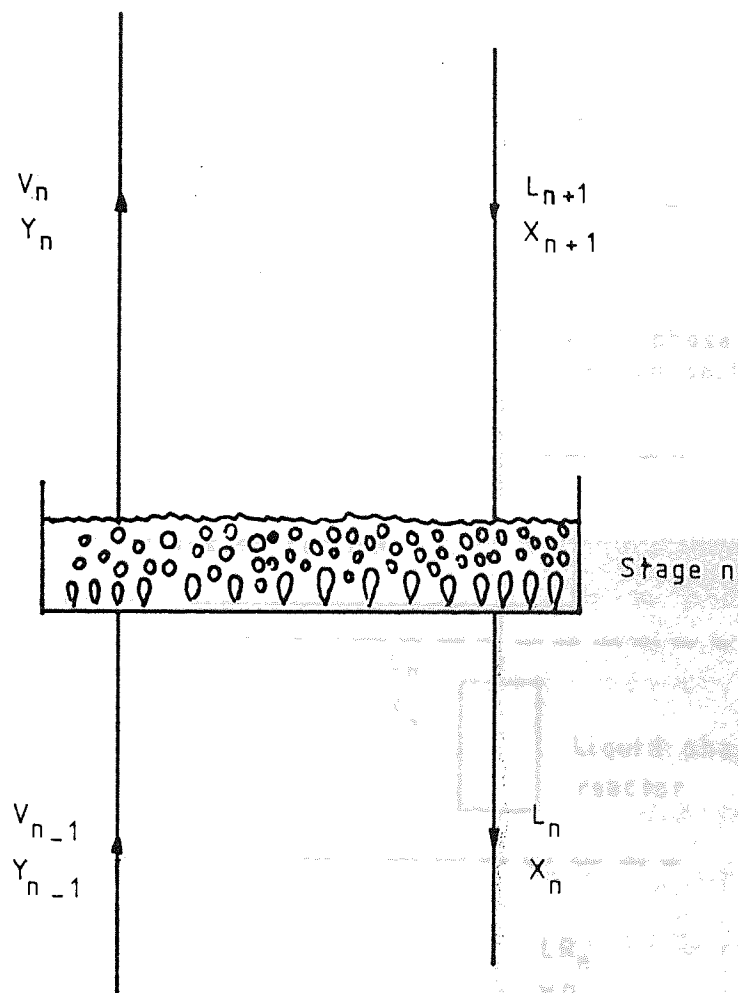


Figure 4.2 Schematic diagram of a distillation tray

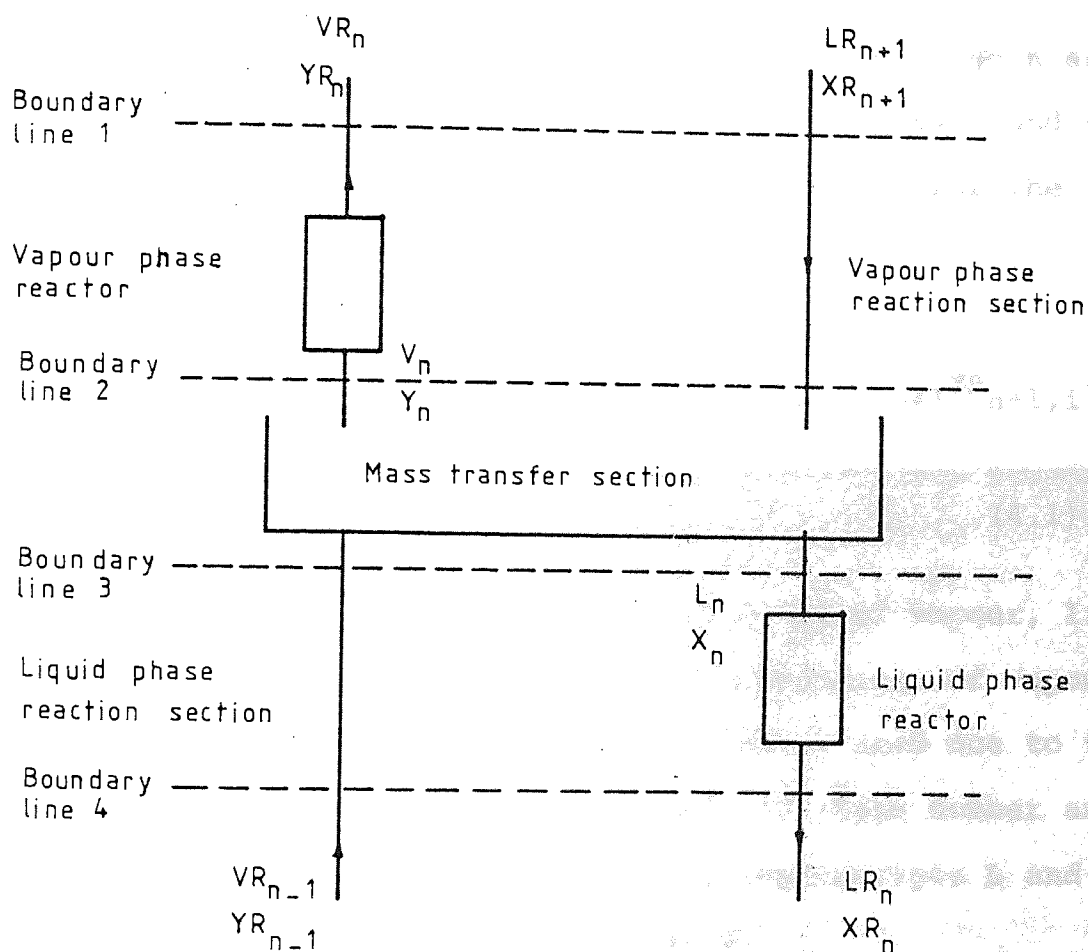


Figure 4.3 Schematic diagram of
distillation tray and
reaction zones

were obtained using the tridiagonal matrix method due to the instability of the numerical solution. However, the procedure and the model are briefly reviewed in this section.

The component mass balance around the stage n as shown in figure 4.3 between the boundary lines 1 and 4 can be written to provide the basic equation for the calculation.

$$V R_{n,i} Y_{n,i} + L R_{n,i} X_{n,i} + r_{n,i}^V + r_{n,i}^L = V R_{n+1,i} Y_{n+1,i} + L R_{n+1,i} X_{n+1,i} + F_{n,i} X_{F,n,i} \quad (4.1)$$

$V R$, $L R$ and F denote the molar flow rates of vapour, liquid and feed, $Y R$ and $X R$ denote the mole fractions of vapour and liquid and r denotes the number of moles used due to the reaction. The subscript n denotes the stage number and i denotes the component number. The superscripts L and V denote the liquid and vapour phases.

Equation 3.18 is applied to stage n in the form of equation 4.2

$$\phi_{n,i} Y_{n,i}^P = \gamma_{n,i} X_{n,i} f_{n,i}^{OL} \quad (4.2)$$

Equation 4.2 is rearranged into equation 4.3 where $K_{n,i}$ the distribution constant of the component i in stage n , equations 4.4 and 4.5 are obtained.

$$YR_{n,i} = \frac{\gamma_{n,i} f_{n,i}^{OL}}{\phi_{n,i} P} X R_{n,i} \quad (4.3)$$

$$Y R_{n,i} = K_{n,i} X R_{n,i} \quad (4.4)$$

$$\text{where } K_{n,i} = \frac{\gamma_{n,i} f_{n,i}^{OL}}{\phi_{n,i} P} \quad (4.5)$$

Equation 4.4 can be applied to stage n-1 in the form of equation 4.6

$$Y R_{n-1,i} = K_{n-1,i} X R_{n-1,i} \quad (4.6)$$

When equations 4.4 and 4.6 are substituted into equation 4.1 for $Y R_{n-1,i}$ and $Y R_{n,i}$ and rearranged, the following relationship is obtained

$$-V R_{n-1} K_{n-1,i} X R_{n-1,i} + (V R_n K_{n,i} + L R_n) X R_{n,i} - L R_{n+1} X R_{n+1,i} = F_n X F_{n,i} - r_{n,i}^V - r_{n,i}^L \quad (4.7)$$

Equation 4.7 can be written in a general form because it can be applied to all stages and each equation is in terms of liquid phase mole fractions of the stage considered and the stages above and below stage n.

$$A_n X R_{n-1,i} + B_n X R_{n,i} + C_n X R_{n+1,i} = D_{n,i} \quad (4.8)$$

$$\text{where } A_n = -V R_{n-1} K_{n-1,i} \quad (4.9)$$

$$B_n = V R_n K_{n,i} + L R_n \quad (4.10)$$

$$C_n = LR_{n+1} \quad (4.11)$$

$$D_n = F_n X F_{n,i} - r_{n,i}^V - r_{n,i}^L \quad (4.12)$$

These equations are modified for the boiler and condenser stages due to the different patterns of flow.

For the boiler stage

$$A_1 = 0 \quad (4.13)$$

$$B_1 = VR_1 K_{1,i} + LR_1 \quad (4.14)$$

$$C_1 = LR_2 \quad (4.15)$$

$$D_1 = -r_{1,i}^V - r_{1,i}^L \quad (4.16)$$

and for the condenser stage

$$A_N = VR_{N-1} K_{N-1,i} \quad (4.17)$$

$$B_N = LR_N \quad (4.18)$$

$$C_N = 0 \quad (4.19)$$

$$D_N = -r_{N,i}^L \quad (4.20)$$

where N is the total number of stages.

Therefore the equations for the N stages would be as follows

$$B_1 X_{R1,i} + C_1 X_{R2,i} = D_1$$

$$A_2 X_{R1,i} + B_2 X_{R2,i} + C_2 X_{R3,i} = D_2$$

$$A_3 X_{R2,i} + B_3 X_{R3,i} + C_3 X_{R4,i} = D_3$$

$$A_N X_{R,N-1,i} + B_N X_{R,N,i} = D_N$$

(4.21)

The above set of equations can be written in matrix form, where the resulting tridiagonal matrix is

$$\begin{bmatrix} B_1 & C_1 & & \\ A_2 & B_2 & C_2 & \\ & A_3 & B_3 & C_3 \\ & & & A_N & B_N \end{bmatrix} \times \begin{bmatrix} X_{R1,i} \\ X_{R2,i} \\ X_{R3,i} \\ X_{R,N,i} \end{bmatrix} = \begin{bmatrix} D_1 \\ D_2 \\ D_3 \\ D_N \end{bmatrix} \quad (4.22)$$

A matrix in the form of equation 4.22 can be written and therefore for a system of m components, m tridiagonal matrix would have to be solved for the liquid mole fractions.

The calculations are followed by the use of already evaluated $X_{Rn,i}$ values to determine the new values for the matrix coefficients A, B, C and D and thus the calculations are iterated to an agreeable solution.

The values of $Y_{Rn,i}$ and T_n can be calculated using

the values of $XR_{n,i}$ and equation 4.4 using the pressure through the phase equilibria relationships as explained in Chapter 3. Thus a new vapour phase concentration profile and temperature profile is obtained. In the early iterations, since the values of $XR_{n,i}$ are calculated from matrix coefficients based on the initial guesses, values of greater than one may be obtained. The solution can be accelerated by normalisation of the calculated $XR_{n,i}$ values and when the solution is approached the effect of normalisation is proportionally reduced. At the solution when the sum of the liquid mole fractions for each stage is unity the values of the calculated $XR_{n,i}$ are not changed by the normalisation procedure.

The calculations are followed by estimating a new profile for the vapour and liquid flow rates throughout the column. A total mass balance is made between the boundary lines 1 and 4 resulting in equation 4.23.

$$VR_n + LR_n + R_n^V + R_n^L = VR_{n-1} + LR_{n+1} + F_n \quad (4.23)$$

Equation 4.24 is derived from rearranging this equation and evaluating LR_{n+1} .

$$LR_{n+1} = VR_n + LR_n + R_n^V + R_n^L - VR_{n-1} - F_n \quad (4.24)$$

Equation 4.25 is formed by making an energy balance around the stage n.

$$VR_n H_n^V + LR_n H_n^L - HR_n^V - HR_n^L = VR_{n-1} H_{n-1}^V + LR_{n+1} H_{n+1}^L + F_n H_n^F + Q_n \quad (4.25)$$

where H is the enthalpy term and HR is the heat of the reaction generated from the reactions in liquid and vapour phases. The term Q_n is referred to as the heat input to the stage.

When equation 4.24 is substituted into equation 4.25 and rearranged the following relationship is obtained.

$$VR_n = \frac{[VR_{n-1} (H_{n-1}^V - H_{n+1}^L) + LR_n (H_{n+1}^L - H_n^L) + F_n (H_n^F - H_{n+1}^L) + HR_n^V + HR_n^L + (R_n^V + R_n^L) H_{n+1}^L + Q_n]}{H_n^V - H_{n+1}^L} \quad (4.26)$$

The values of Q_n and F_n are set equal to zero when there is no heat or feed input to the system.

Starting the calculation for VR_n and LR_n from the bottom of the column, VR_1 can be calculated from equation 4.26 where LR_1 is known and is equal to the flow rate of the bottom product. The term VR_{n-1} for the boiler stage is set equal to zero. Some variables in equation 4.26 such as the heat input to the boiler, feed flow rate, feed composition, feed plate position and feed enthalpy, are specified for a particular experiment. The current calculated variables are used for the rest of the variables such as the temperature profile, composition

profile and number of reacted moles on each plate. These variables are used to calculate the enthalpy terms and the heat of reactions. Once VR_1 is calculated equation 4.24 can be used to evaluate LR_2 . The calculations are continued utilising VR_n and LR_{n+1} to evaluate VR_{n+1} and LR_{n+2} until all the VR and LR values are calculated.

The number of moles reacted in the vapour and liquid phases on each stage have now to be evaluated. The already calculated values of the different variables are utilised to calculate the reacted number of moles.

In order to calculate the number of moles reacted in the liquid phase on stage n a component mass balance between the boundary lines 1 and 3 is set up

$$VR_n YR_{n,i} + L_n X_{n,i} + r_{n,i}^V = VR_{n-1} YR_{n-1,i} + LR_{n+1} XR_{n+1,i} + F_n XF_{n,i} \quad (4.27)$$

where L_n and $X_{n,i}$ are the flowrate and mole fractions of liquid entering the liquid phase reactor on stage n and $r_{n,i}^V$ is the number of moles of component i reacted in the vapour phase on stage n. Equation 4.27 is rearranged to evaluate $x_{n,i}$

$$X_{n,i} = \frac{VR_{n-1} YR_{n-1,i} + LR_{n+1} XR_{n+1,i} + F_n XF_{n,i} - VR_n YR_{n,i} - r_{n,i}^V}{L_n} \quad (4.28)$$

The values of $X_{n,i}$ can be calculated for all the components.

in stage n using equation 4.28. A total mass balance is taken between the boundary lines 3 and 4 in Figure 4.2.

$$L_n = LR_n + L_n \alpha_n^L + L_n \beta_n^L \quad (4.29)$$

Equation 4.29 is rationalised to evaluate L_n

$$L_n = \frac{LR_n}{1 - \alpha_n^L - \beta_n^L} \quad (4.30)$$

The values of α_n^L and β_n^L can be calculated from the equations I.6 and I.7 in Appendix I, using the calculated values of $X_{n,i}$. The values of L_n can be calculated by substitution of the values of LR_n , α_n^L and β_n^L into equation 4.30. The values of $r_{n,i}^L$ are calculated from equations 4.31 to 4.35.

$$r_{n,1}^L = L_n (\alpha_n^L + \beta_n^L) \quad (4.31)$$

$$r_{n,2}^L = -L_n \beta_n^L \quad (4.32)$$

$$r_{n,3}^L = L_n \beta_n^L \quad (4.33)$$

$$r_{n,4}^L = -L_n \alpha_n^L \quad (4.34)$$

$$r_{n,5}^L = L_n \alpha_n^L \quad (4.35)$$

The values of R_n^L can be calculated from equation 4.36 which is the sum of equations 4.31 to 4.35.

$$R_n^L = L_n (\alpha_n^L + \beta_n^L) \quad (4.36)$$

The heat of reaction for the liquid phase reaction can now be calculated knowing the values of R_n^L and the molar heat of reaction.

A similar calculation procedure is used for the vapour phase with the total mass balance between the boundary lines 2 and 4 given by equation 4.37.

$$V_n Y_{n,i} + L R_{n,i}^{XR} + r_{n,i}^L = V_{n-1} Y_{n-1,i} + L R_{n+1,i}^{XR} + F_n X_{n,i}^F \quad (4.37)$$

Equation 4.37 is solved for $Y_{n,i}$ to give equation 4.38

$$Y_{n,i} = \frac{V_{n-1} Y_{n-1,i} + L R_{n+1,i}^{XR} + F_n X_{n,i}^F - L R_{n,i}^{XR} - r_{n,i}^L}{V_n} \quad (4.38)$$

Equations I.10 and I.11 are used to calculate α_n^V and β_n^V utilising the values of $Y_{n,i}$ calculated from equation 4.38. The value of V_n can be calculated from equation 4.39 which is later used to calculate $r_{n,i}^V$ values through equations 4.40 to 4.44

$$V_n = \frac{V_{n-1}}{1 - \alpha_n^V - \beta_n^V} \quad (4.39)$$

$$r_{n,1}^V = V_n (\alpha_n^V + \beta_n^V) \quad (4.40)$$

$$r_{n,2}^V = -V_n \beta_n^V \quad (4.41)$$

$$r_{n,3}^V = V_n \beta_n^V \quad (4.42)$$

$$r_{n,4}^V = -V_n \alpha_n^V \quad (4.43)$$

$$r_{n,5}^V = V_n \alpha_n^V \quad (4.44)$$

The value of R_n^V can be calculated from equation 4.45 which is the sum of equations 4.40 to 4.44. The heat of reaction can also be calculated, knowing the molar heat of reaction for the vapour phase.

$$R_n^V = V_n (\alpha_n^V + \beta_n^V) \quad (4.45)$$

The calculated values are then used to redefine the coefficients of the tridiagonal matrix and the calculations are repeated until convergence is achieved. The calculation procedure can be best explained by the following steps.

1. Estimate the initial guesses for the start of calculations.
2. Calculate the coefficients of the tridiagonal matrix.
3. Evaluate the liquid mole fractions from the solution of tridiagonal matrix.
4. Calculate the vapour phase mole fractions and temperatures.
5. Evaluate the vapour and liquid flow rates and component distribution constants.

6. Calculate the intermediate values for calculation of number of moles reacted on each stage.
7. Convergence check.
8. If no convergence is achieved the calculations are repeated from step 2.

A computer program was written in FORTRAN for the distillation of formaldehyde, water and methanol, employing the explained method. The tridiagonal method was found to be highly unstable for this system. Modification of initial guesses was found to be unhelpful and had no significant effect on the convergence of the calculations. It was observed from a study of the intermediate calculated results from the computer program that in each iteration the computed results were further away from the true solution. Although several combination of equations for mass and energy balance were tried in different programs, no numerical convergence was achieved. The numerical instability in this method is thought to be caused by the effect of calculating the reacted number of moles on the coefficients of tridiagonal matrix, which in turn resulted in the negative values for the mole fractions of the liquid phase after only a few iterations.

4.3.2 Stage to Stage Method

A different method of solution had to be adopted to model the distillation of formaldehyde, because a convergent solution, using the tridiagonal matrix method combined with the proposed model for each stage could not be achieved. Further, the model for the distillation stage had to be simplified by assuming only a liquid phase reaction took place. The fact that a chemical reaction takes place in the vapour phase is not changed by this simplifying assumption. The explanation can be given by imposing a further constraint to the mass transfer section of the distillation stage model, by assuming that the mass transfer for the vapour phase is evolved until the chemical and phase equilibrium are reached simultaneously. This can be explained further by considering the entering vapour to the distillation stage which is in chemical equilibrium as the amount of mass transferred to or from this vapour phase would keep the vapour phase at chemical equilibrium. The composition of the vapour phase is changed in the mass transfer section of the amount of mass transferred is enough to maintain the chemical equilibrium throughout the transition of vapour phase composition. Therefore, if the composition of the vapour phase is always kept at chemical equilibrium in the mass transfer section by

removing or introducing mass from the liquid phase, no chemical reaction would occur after the mass transfer section, since the composition of vapour phase would already be at chemical equilibrium at the temperature of the stage.

However, this assumption would imply that the liquid phase composition would have to be altered from the entering composition which is at chemical equilibrium to compensate for the change in the vapour phase composition. Therefore the liquid leaving the mass transfer section would no longer be at the chemical equilibrium. The liquid phase is then passed through the liquid phase reactor section to react to a new equilibrium at the temperature of the stage.

Therefore using this assumption, the irregularity from the vapour phase has been transferred into the liquid phase and as a consequence the definition of α_n^V and β_n^V is not required in the new model.

Thus a stage to stage method of calculation for the distillation of formaldehyde solutions has been adopted for the calculations instead of the tridiagonal matrix method. The performance of the calculations can easily be analysed in this method, since each stage is calculated separately and therefore the current variables calculated in each stage can be observed and traced during

the course of the calculations.

The diagram of the proposed model for the distillation stage is shown in figure 4.4. The stage to stage calculations are carried out for each distillation stage starting from the bottom of the column. In each stage the calculations are iterated until the current solution is reached, using the calculated variables from the previous iterations. The calculation is moved to the next stage and repeated in a similar manner. When the top stage is reached the calculation is transferred to the bottom stage and the whole calculations are repeated until no change is observed in two successive iterations. The calculation is carried out by two different iterations. The inner iteration is for the calculation of each individual stage. The outer iteration is used for repeating the calculation throughout the column from bottom to the top. Similarly in this method of solution the iteration on the vapour mole fraction and temperature was kept separate from the column calculations.

Initial guesses for the temperature profile, vapour composition, liquid composition, vapour flow rates and number of reacted moles in the liquid phase for each stage are used to start the calculation. Similar specified variables to those described in section 4.3 have been used. In this method the calculation is started from the bottom stage of the column and therefore in a typical

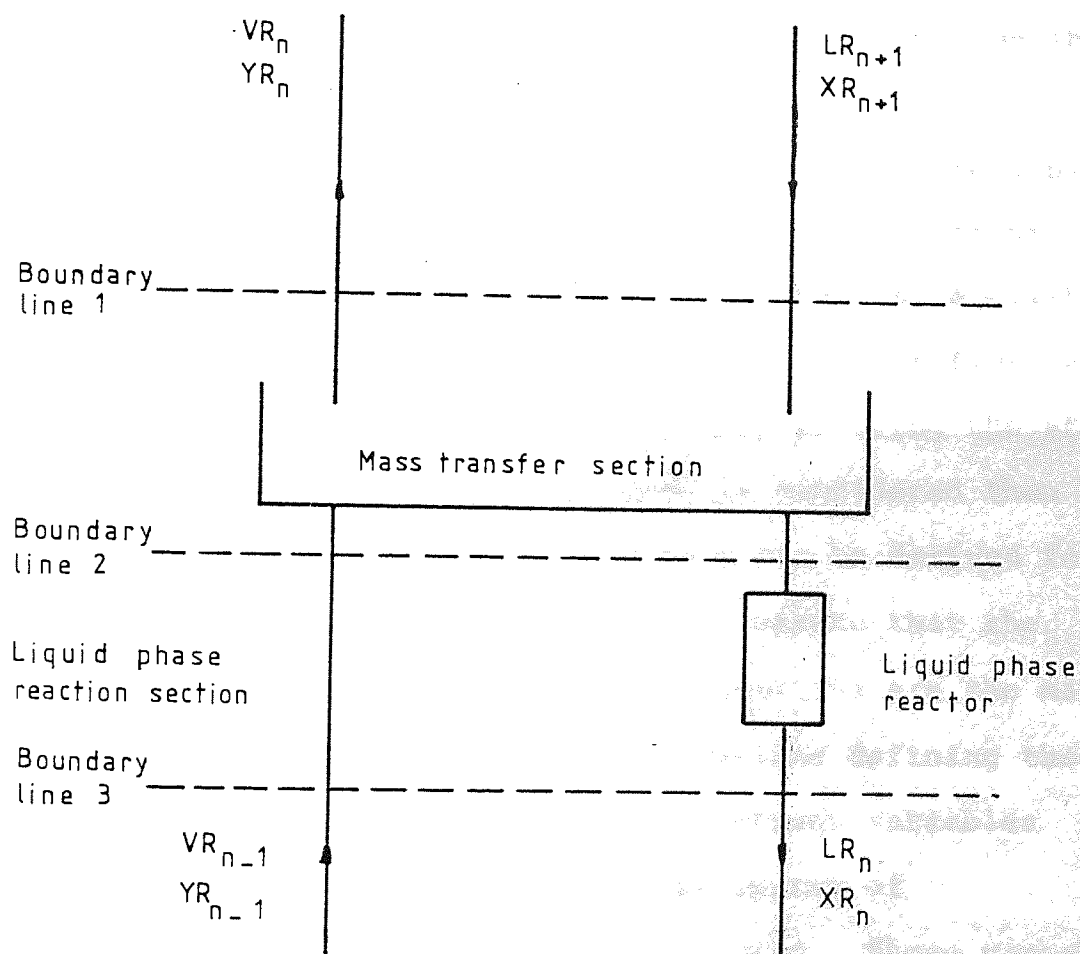


Figure 4.4 Schematic diagram of distillation tray with liquid phase reaction zone

stage the variables in the lower part of the stage should either be known as, in the case of reboiler, or already evaluated from the calculation of the previous stage. In Figure 4.4, VR_{n-1} , LR_n and their compositions are known and utilising the vapour-liquid equilibrium section the composition of the vapour phase leaving stage n , the temperature of stage n can be calculated. The remaining unknown variables for stage n are the composition of liquid entering the stage which is in chemical equilibrium, the number of moles reacted in stage n , vapour flow rate leaving the stage and liquid flow rate entering the stage. If the number of unknown variables is considered then the same number of independent equations can be derived for stage n and care should be taken to ensure that the problem is not over defined. The equations are the mass balance, the energy balance and equations defining the chemical reactions. The number of unknown variables for each distillation stage for the system of formaldehyde, water and methanol is nine. These variables are the number of moles reacted in the first reaction, the number of moles reacted in the second reaction, the flow rate of the entering liquid, the flow rate of the leaving vapour and five variables defining the mole fraction of components in the entering liquid phase.

The liquid stream entering stage n is assumed to be in

chemical equilibrium and therefore equations 4.46 and 4.47 should be satisfied by the liquid mole fractions of the components. The relationships for the chemical reaction are defined in these equations in terms of the chemical reaction constants for the hydration of formaldehyde in equation 4.46 and the reaction of formaldehyde with methanol in equation 4.47. These equations are explained in detail in Appendices I and II.

$$K_1^L = \frac{X_{n+1,1}^{R}}{X_{n+1,4}^{R}} \quad (4.46)$$

$$K_2^L = \frac{X_{n+1,2}^{R}}{X_{n+1,1}^{R} X_{n+1,3}^{R}} \quad (4.47)$$

The sum of the mole fractions for the liquid phase entering stage n should be equal to one. This constraint is expressed by equation 4.48.

$$\sum_{i=1}^5 X_{n+1,i}^{R} = 1 \quad (4.48)$$

A component mass balance between the boundary lines 1 and 3 can be carried out resulting in equations 4.49 - 4.53.

$$L_{n+1} X_{n+1,1}^{R} + V_{n-1} Y_{n-1,1}^{R} + F X_{n,1}^{F} = L_n X_{n,1}^{R} + V_n Y_{n,1}^{R} + \alpha_n^L + \beta_n^L \quad (4.49)$$

$$L_{n+1} X_{n+1,2}^{R} + V_{n-1} Y_{n-1,2}^{R} + F X_{n,2}^{F} = L_n X_{n,2}^{R} + V_n Y_{n,2}^{R} - \beta_n^L \quad (4.50)$$

$$L_{n+1} X_{n+1,3}^{R} + V_{n-1} Y_{n-1,3}^{R} + F X_{n,3}^{F} = L_n X_{n,3}^{R} + V_n Y_{n,3}^{R} + \beta_n^L \quad (4.51)$$

$$LR_{n+1}^{XR} + VR_{n-1}^{YR} + F_n^{XF} = LR_n^{XR} + VR_n^{YR} - \alpha_n^L \quad (4.52)$$

$$LR_{n+1}^{XR} + VR_{n-1}^{YR} + F_n^{XF} = LR_n^{XR} + VR_n^{YR} + \alpha_n^L \quad (4.53)$$

The final equation for the set of equations for stage n is provided by an energy balance over stage n

$$LR_{n+1}^{HL} + VR_{n-1}^{HV} + F_n^{HF} = LR_n^{HL} + VR_n^{HV} - Q_n + \alpha_n^L hrl_n^L + \beta_n^L hr2_n^L \quad (4.54)$$

where hrl_n^L is defined as the molar heat of reaction for the hydration of formaldehyde and $hr2_n^L$ is defined as the molar heat of reaction for the reaction of formaldehyde with methanol. The liquid phase is denoted by the superscript L.

The enthalpy of liquid entering stage n, H_{n+1}^L , is a function of composition and temperature of the liquid stream entering stage n. The liquid phase enthalpy for stream LR_{n+1} can be defined in terms of the compositions by using the simple mixing rule as in equation 4.55.

$$H_{n+1}^L = h1^{XR} + h2^{XR} + h3^{XR} + h4^{XR} + h5^{XR} \quad (4.55)$$

The enthalpies of pure liquid formaldehyde, hemiformal, methanol, methylene glycol and water are given by the coefficients h1 to h5 in equation 4.55. The enthalpy of a pure liquid is a function of temperature and the

dependence of enthalpy on temperature is discussed in Appendix V.6. When equation 4.55 is substituted into equation 4.54, a more practical equation for the solution of the distillation process on stage n is achieved.

$$\begin{aligned} & h_1 L_{n+1} X_{n+1,1} + h_2 L_{n+1} X_{n+1,2} + h_3 L_{n+1} X_{n+1,3} + h_4 L_{n+1} X_{n+1,4} + \\ & h_5 L_{n+1} X_{n+1,5} + V_{n-1} H_{n-1}^V + F_n H_n^L - L_n H_n^L - V_n H_n^V + Q_n - \alpha_n h_{r1} L_n^L - \beta_n h_{r2} L_n^L = 0 \end{aligned} \quad (4.56)$$

The mathematical relationships for stage n are represented by the nine equations 4.46-4.53 and 4.56. A unique real solution for each plate for a set of initial information would be provided by the simultaneous solution of these equations. The equations are solved first by evaluating the coefficients of the variables in the equations. Some initial information is needed to calculate these coefficients. The temperature profile, vapour and liquid composition profile, vapour and liquid flow rates and number of moles reacted in each stage are utilised as the guessed information. These parameters are recalculated in each iteration. The solution is reached when no change is observed in the calculated variables in two successive iterations.

All the nine equations are nonlinear except equation 4.48 and thus conventional methods for the solution of simultaneous equations can not be applied. Generally an

iterative solution of the linearised form of the equations can be used for the solution of nonlinear simultaneous equations. The Newton-Raphson method of solution for simultaneous nonlinear equations has been applied for the solution of the above set of equations.

The linearised form of the equations are solved by using the Gauss elimination techniques. A new guess is provided by the solution of these equations and these variables are used to update the coefficients of the linearised equations matrix. The solution is iterated until the convergence is achieved to a set of results for the nonlinear set of equations. The procedure and methods for the Newton-Raphson method are described in Appendix IX.

Finally the information about the vapour leaving stage n and the liquid entering stage n is provided by the iterative solution of the nine nonlinear simultaneous equations for each stage. The calculated information is used for stage $n+1$ because the vapour leaving stage n is the vapour entering stage $n+1$ and the liquid entering stage n is the liquid leaving stage $n+1$. The composition of liquid is used to calculate the stage temperature and the composition of the vapour leaving the stage. These values are used to calculate the coefficients of the set of simultaneous equations. Thus the calculations are carried out until the condenser stage is reached. The

calculations are repeated starting from the reboiler stage using the information calculated in the previous iteration and the iterations are halted when the difference between the calculated variables in the two iterations are within a preset tolerance limit.

The calculation can be explained by the following steps.

1. Estimate the initial guess to start the calculations.
2. Start the calculations from the bottom of the column.
3. Set up the simultaneous equations.
4. Solve the simultaneous equations.
5. Find the composition of vapour leaving the stage and the temperature of the stage.
6. Check if convergence is reached, if not start from step 3.
7. Check for the convergence of the solution, otherwise start from step 2.
8. End of the calculations.

4.3.2.1 Reboiler Stage

The equations for the reboiler stage are similar to any other stage except that there is no vapour entering this stage. The terms to include the heat input or output from the stage are contained in all the equations used for the calculation and provision is made to include the possibility of selecting the feed plate position. Multiple

feed processes can be accommodated if at the start of the program their position is specified. The program also can be easily modified to allow for side stream withdrawals.

4.3.2.2 Condenser Stage

The equations for the condenser stage are different from the equations specified for stage n in the column because there is no vapour output and liquid input to this stage. The vapour is assumed to condense completely in this stage. The equations are determined by the total mass balance, the chemical reaction equilibrium relationships and the energy balance equations for this stage.

In the condenser the following sequence of events has been assumed (see Figure 4.5). First the vapour phase is condensed to the liquid phase. Because the reaction constants are different in the vapour and liquid phases, the composition of the condensed liquid which was in chemical equilibrium according to the vapour phase reaction constant, would have to be changed to compositions which are in chemical equilibrium in the liquid phase by a further reaction.

Equations 4.57 to 4.59 can be formulated for this scheme.

$$\alpha_N^L = \frac{V_{R,N-1} Y_{R,N-1,1} - \beta_N^L - K_{N,1}^L V_{R,N-1} Y_{R,N-1,4}}{K_{N,1}^L + 1} \quad (4.57)$$

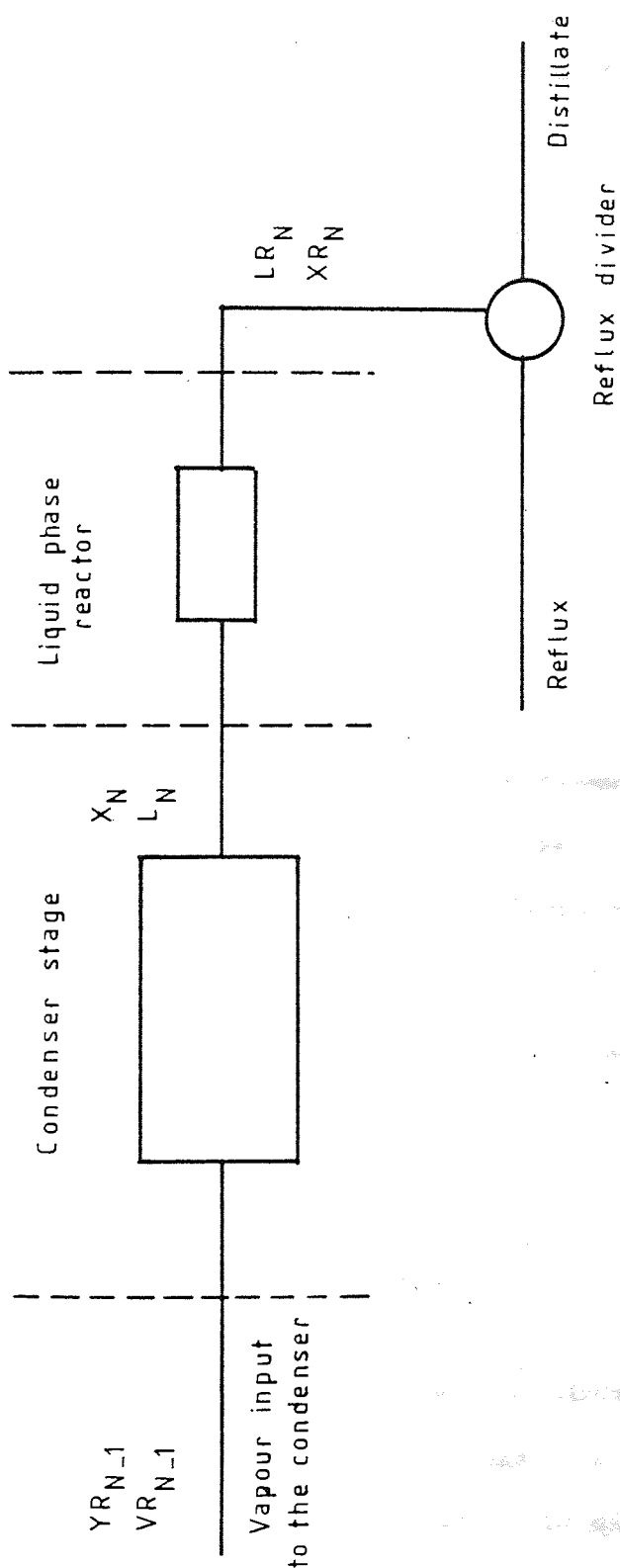


Figure 4.5. Schematic diagram of condenser stage

$$VR_{N-1} = L_N + \alpha_N \frac{L_N}{V_N} + \beta_N \frac{L_N}{V_N} \quad (4.58)$$

$$VR_{N-1} H_{N-1}^V = L_N H_N^L + \alpha_N \frac{L_N}{V_N} H_{N-1}^V + \beta_N \frac{L_N}{V_N} H_{N-1}^V + Q_N \quad (4.59)$$

The applied form of equation I.6 is modified for this stage to give equation 4.57. Since the molar flow rate of the vapour into this stage would be equal to the composition of liquid phase before the reaction. This can be explained further by formulating a mass balance on the boundary lines 1 and 2 in Figure 4.5.

Equation 4.58 can be obtained by formulating a mass balance between boundary lines 2 and 3. Equation 4.59 can then be obtained by formulating an energy balance between the boundary lines 1 and 3.

The solution for the condenser stage can be obtained from the simultaneous solution of these three linear equations using the Gauss elimination technique.

4.4 PLATE EFFICIENCY

The Murphree and overall column efficiency are the most widely used definitions for the efficiency of a distillation process, when no experimental data is available. The efficiency of a single tray is given by the Murphree plate efficiency whilst the column efficiency is used for the complete column. The Murphree efficiency

can be expressed in terms of the liquid or vapour phase compositions. In this work the Murphree vapour efficiency has been used because of the wide use of this definition and the availability of various correlations for the calculation of this term.

The vapour phase Murphree efficiency is defined as the ratio of the actual change in the vapour composition caused by the vapour passing through a tray to the composition change which the vapour would attain if it was discharged from the tray in equilibrium with the liquid leaving the same tray.

The overall efficiency is defined as the ratio of the number of theoretical trays required for a specific separation to the number of actual trays required for the same separation.

The Murphree efficiency may be applied either to the whole tray or to a point on the tray. The Murphree vapour efficiency, E_{mv} , of the entire tray for stage n , is defined by equation 4.60.

$$E_{mv} = \frac{Y_n - Y_{n-1}}{Y_n^* - Y_{n-1}} \quad (4.60)$$

where Y_n and Y_{n-1} are the vapour mole fractions for the streams leaving stage n and stage $n-1$ respectively and Y_n^* is the mole fraction of vapour in equilibrium with

liquid leaving tray n . The Murphree point efficiency for the vapour phase can be defined by a similar equation except that Y_n, Y_{n-1} and Y_n^* are defined as the vapour mole fractions at the point being considered on the plate.

The efficiency can be used in the calculations if it is defined in terms of parameters which depend on the physical properties of the system. Several methods have been developed for calculating the plate efficiency and these have been discussed earlier in section 4.2.2.

The most extensive work on the prediction of plate efficiencies can be found in the A.I.Ch.E. manual (133). The methods which have been developed later have been based mainly on the theory used in the A.I.Ch.E. Bubble Tray Design Manual.

Although sieve plates are one of the most commonly used types of distillation trays, the correlations available for predicting the efficiency of sieve plates are much more limited in their application than those available for bubble trays.

It was originally planned to avoid the use of efficiency prediction methods in this work as the accuracy of such methods in a reacting system is questionable. It was thought that the experimental Murphree efficiencies could be evaluated by measuring the vapour and liquid compositions at total reflux. The experimental Murphree efficiencies

could then have been used to obtain a correlation for the calculation of Murphree efficiencies, using a regression algorithm technique. The correlations would have been similar to those proposed by the A.I.Ch.E. manual as used by Olsson and Svensson (73) for the formaldehyde-water system. However, it was found that accurate experimental vapour phase compositions could not be obtained from the condensation of the vapour samples taken from the distillation column. Large errors in the measurement of the vapour phase compositions were caused by the escape of free formaldehyde from the condensation chamber or the polymerisation of formaldehyde in the condensed liquid due to the low temperature in the condensation chamber. As a result one of the efficiency prediction methods had to be included in the mathematical model.

The method proposed by Diener and Gerster (143) is based on the A.I.Ch.E. method using the matrix relationships in order to extend the use of the method for multicomponent systems. This method has been successfully applied to some ternary systems (143, 144). Lengthy and complex matrix computations are involved in this method. Since the solution of the distillation column was based on two different iterations, one on the whole distillation column and one on each plate, the efficiency factors would have to be calculated several times for each stage. Therefore the computation time for the distillation column would be

increased exponentially with an increase in the number of plates.

Due to the lack of data for certain components in the system, some of the properties have to be estimated through the use of the generalised prediction methods. Some error is introduced by the application of these prediction methods for the estimation of the physical properties necessary to calculate the efficiency factors. The accuracy of these methods are between 3% to 20% depending on the method and the estimated property. Thus some deviations from the actual efficiencies are expected from the Diener and Gerster method particularly as the performance of this method for reacting multicomponent systems is not very well known.

Although the A.I.Ch.E. method suffers from a similar lack of accurate physical properties for this system the method has been found to be more simple with almost the same accuracy. Therefore the A.I.Ch.E. method was applied for the efficiency calculation in the distillation column, using certain modifications.

4.4.1 A.I.Ch.E Method of Plate Efficiency Calculations

The A.I.Ch.E. method for predicting plate efficiency was developed essentially for binary mixtures on bubble cap trays although the method was later extended to other types of trays. The basic equations used in developing

the method are derived from the traditional diffusion and mass transfer equation. Three main assumptions are involved in deriving the equations.

1. The rate of mass transfer of a component within a phase is proportional to the difference in the concentration or partial pressure of a component in the bulk of the phase and at the interface.
2. Equilibrium exists between the phases at the interface.
3. The hold-up of the transferring component in the boundary layer or region near the phase boundary is negligible with respect to the amount transferred in the process.

The resistance in the phases are added to represent the overall resistance in the mass transfer process.

$$\frac{1}{NOG_{n,i}} = \frac{1}{NG_{n,i}} + \frac{RA_{n,i}}{NL_{n,i}} \quad (4.61)$$

where

$$RA_{n,i} = \frac{SL_{n,i} VR_n}{LR_n} \quad (4.62)$$

The relationship between the NOG and the point efficiency is given by equation 4.63.

$$EO_{n,i} = 1 - \text{Exp}(-NOG_{n,i}) \quad (4.63)$$

4.4.2 Efficiency Calculations for Formaldehyde Solutions

The plate efficiency calculations for the formaldehyde-methanol-water system can be carried out in two different ways based on the A.I.Ch.E. manual method.

The first procedure is similar to the method used by Olsson and Svensson (73) for the formaldehyde-water system. However, only the plate efficiencies for the formaldehyde-methanol-water system can be calculated using this method and thus the products of the reactions of formaldehyde with methanol and water have to be ignored. Furthermore the gradient of the vapour liquid equilibrium curve and vapour and liquid flow rates which are parameters for the plate efficiency calculations, could not be accurately calculated for the ternary system, as the vapour and liquid compositions and flow rates are calculated for the quinary system and not for the ternary system.

The second procedure is based on the application of the correlations for the quinary system of formaldehyde, hemiformal, methanol, methylene glycol and water. This procedure is thought to be more accurate than the first procedure because a better representation of the theory of the system is obtained. Although more and longer calculations are needed because of the two extra components, the second procedure was applied for the calculation of plate efficiencies.

The plate efficiency calculations can be explained by the following steps.

1. The vapour rate based on the bubbling area.

A uniform bubbling pattern is assumed across the plate. This can be substantiated by visual observations of the distillation plates where a uniform bubbling mixture was formed on each plate. In the design of the column, the weirs and downcomers were located outside the column and therefore did not interfere with the flow patterns on the trays. The bubbling area, therefore is equal to the cross sectional area of the column and the vapour rate is calculated from equation 4.64.

$$UG_n = \frac{V_{mix_n} \cdot VR_n}{S} \quad (4.64)$$

where

UG_n = vapour rate ($m \min^{-1}$)

VR_n = molar flow rate of vapour ($moles \min^{-1}$)

V_{mix_n} = molar volume of vapour ($m^3 \text{ mole}^{-1}$)

S = cross section area (m^2)

2. F factor

This factor is calculated from equation 4.65.

$$FF_n = UG_n V_n^{1/2} \quad (4.65)$$

where

ρ_n^V = the vapour density (kg m^{-3})

and

$$\rho_n^V = (30YR_{n,1} + 62YR_{n,2} + 32YR_{n,3} + 48YR_{n,4} + 18YR_{n,5}) \times 1000 / V_{\text{mix}_n} \quad (4.66)$$

3. The liquid rate per width of the plate, LF

An average width is defined for the column because of the circular cross section. The average is taken between the liquid inlet diameter and the column diameter in the form of equation 4.67.

$$w = \frac{d_i + d_c}{2} \quad (4.67)$$

where d_i and d_c are the liquid inlet diameter and the column diameter respectively and w is the average width of the column.

The liquid molar volume for the mixture is calculated by the contribution of each component from equation 4.68.

$$L_{\text{mix}_n} = LM_{n,1} X_{R,n,1} + LM_{n,2} X_{R,n,2} + LM_{n,3} X_{R,n,3} + LM_{n,4} X_{R,n,4} + LM_{n,5} X_{R,n,5} \quad (4.68)$$

where $LM_{n,i}$ is the molar volume of liquid component i ($\text{cm}^3 \text{ mole}^{-1}$, equivalent to $10^{-6} \text{ m}^3 \text{ mole}^{-1}$).

LF is defined by combining equations 4.67 and 4.68 to

give equation 4.69. When LF is expressed in the units of (US gal/min.ft), a minimum value of 2 is quoted in the A.I.Ch.E. manual

$$LF_n = \frac{L_{mix_n} \cdot LR_n}{w} \quad (4.69)$$

4. The slope of equilibrium curve for a multicomponent system is calculated through equation 4.70, as suggested by the A.I.Ch.E manual.

$$SL_{n,i} = \frac{\gamma_{n-1,i}^{P^S} X_{n-1,i}^{XR} - \gamma_{n,i}^{P^S} X_{n,i}^{XR}}{P(XR_{n-1,i} - XR_{n,i})} \quad (4.70)$$

The values of activity coefficients and vapour pressure are calculated in the vapour-liquid equilibrium section.

5. The value of RA - the ratio of the slope of the equilibrium curve to the operating line slope is calculated through equation 4.62 in the form of equation 4.71.

$$RA_{n,i} = SL_{n,i} \frac{VR_n}{LR_n} \quad (4.71)$$

6. The height of froth for sieve plates was calculated from equation 4.72 (245-6)

$$hf_n = 0.0354 + \frac{4.81}{60} LF_n + 1.05 wh_n + \frac{0.0384}{60} UG_n \quad (4.72)$$

where

hf_n = froth height on plate n (m)

LF_n = liquid volume rate per width of plate
($m^3 \cdot min^{-1} (m \text{ of width})^{-1}$)

wh_n = weir height (m)

UG_n = superficial velocity of vapour ($m \text{ min}^{-1}$)

7. The height of clear liquid for sieve plates was obtained from equation 4.73 (245-6).

$$hL_n = 0.024 + \frac{1.74}{60} L_n + 0.372 wh_n + \frac{0.012}{60} UG_n \quad (4.73)$$

where

hL_n = height of clear liquid (m)

8. The liquid residence time on each plate can be calculated from equation 4.74.

$$tL_n = \frac{hL_n \cdot S}{LR_n V_{mix_n}} \quad (4.74)$$

S = cross sectional area (m^2)

tL_n = liquid residence time (min)

9. The number of liquid phase transfer units can be obtained from equation 4.75 (247).

$$NL_{n,i} = 100 (3.875 DL_{n,i})^{0.5} (0.00669 FF_n + 0.17) tL_n \quad (4.75)$$

where

$DL_{n,i}$ = diffusivity of component in liquid ($\text{cm}^2 \text{s}^{-1}$)

tL = liquid residence time (s)

The value of the liquid phase diffusivity $DL_{n,i}$ can be estimated from the correlations given by Wilke and Chang (248) in the form of equation IV.13.

The viscosity of the liquid is calculated from a polynomial fitted to the solution viscosity in terms of the solution temperature and composition. The method and equations for the calculation of the liquid phase viscosity are discussed in Appendix IV.1.

10. The number of gas phase transfer units can be obtained from the correlation of Jeromin, Holik and Knapp (154).

$$NG_{n,i} = \frac{1}{\sqrt{SC_G}} (0.776 + 0.0457 wh_n - \frac{0.238}{60} FF_n + 1.75 LF_n) \quad (4.76)$$

where

SC_G = vapour phase Schmidt number $\left[\frac{\rho_g D_g}{\mu_g} \right]$

FF_n = The F factor

LF_n = liquid rate per width of tray ($m^3 \text{ min}^{-1} (\text{m of width})^{-1}$)

wh = weir height (cm)

The values of vapour phase diffusivity can be estimated by the correlation of Wilke and Lee (155) in the form of equation IV.14. The diffusion of a component in a mixture can be determined from equation IV.21.

The gas viscosities are calculated from the rigid sphere model (158) by equation IV.7. The viscosity of multicomponent gas mixtures may be explained by the rigorous kinetic theory (164) in the form of equation IV.11.

11. Utilising the values calculated in steps 1 to 10 the value of overall gas transfer unit can be calculated using equations 4.61 and 4.63.

12. The plate efficiency can be determined by taking into account liquid mixing across the plate and the direction of flow of the liquid on successive plates. Because the liquid is not completely mixed, the dimensionless Peclet number is introduced in the A.I.Ch.E manual as the characteristic parameter of the mixing intensity on a plate. This is defined on the ratio of the distance travelled by the liquid to a pseudo-mixing length.

$$Pe = \frac{l^2}{DE.tL} \quad (4.77)$$

where ℓ is the liquid travel across the plate (m) which is assumed to be equal to the diameter of the tray. The value of the eddy diffusion coefficient DE has to be determined from experimental data. It is given by equation 4.78 (154).

$$DE = 0.0929 (0.0124 + \frac{0.0561}{60} U_{Gn} + 0.202 L F_n + 0.00591 \ell w_h)^2 \quad (4.78)$$

The plate efficiency can now be determined from equation 4.79.

$$\frac{E_{n,i}}{EO_{n,i}} = \frac{1 - \exp(-\eta + Pe)}{(\eta + Pe) \{1 + [(\eta + Pe)/\eta]\}} + \frac{\exp(\eta) - 1}{\eta \{1 + [\eta/(\eta + Pe)]\}} \quad (4.79)$$

with

$$\eta = \frac{Pe}{2} \left[\sqrt{1 + \frac{4 \cdot RA \cdot EO}{Pe}} - 1 \right] \quad (4.80)$$

In the plate efficiency calculations the vapour entering the plate is assumed to be completely mixed. This assumption can be made because the diameter of the experimental column, used in this work is quite small compared with industrial columns.

The effect of entrainment and weeping were not considered in the efficiency calculations because by careful maintaining of the experimental conditions weeping

and entrainment were avoided.

However further problems were caused by the A.I.Ch.E. efficiency calculations in the evaluation of the vapour phase compositions. The sum of the calculated vapour phase mole fractions may not add to unity, since all the efficiencies were calculated independently. Thus, the mole fraction of one of the components had to be calculated by difference.

$$Y_{R,n,i} = 1 - \sum_{\substack{j=1 \\ j \neq i}}^m Y_{R,n,j} \quad (4.81)$$

From several experimental executions of the computer programs for the distillation column, it was observed that if the vapour phase mole fraction of water was calculated from equation 4.81 a faster convergence was achieved. However, in order to have a general model for the calculation of the system, provision was made so that the vapour phase mole fraction of any selected component could be calculated using equation 4.81 by adjustment of a flag in the input data for the computer program.

According to the physical properties of the components of a system the point efficiency may be related to only one of the gas or liquid transfer units. In equation 4.61 one of the values of $\frac{1}{N_{G,n,i}}$ or $\frac{R A_{n,i}}{N_{L,n,i}}$ may be much larger than the other. If $\frac{1}{N_{G,n,i}}$ is much larger than $\frac{R A_{n,i}}{N_{L,n,i}}$, the value of $\frac{R A_{n,i}}{N_{L,n,i}}$ becomes negligible and can be ignored.

Such a system is controlled by the vapour film resistance. The opposite is true when $\frac{RA_{n,i}}{NL_{n,i}}$ is much larger and the first term can be neglected, such a system is defined as liquid film controlling. The determination of the controlling film element is affected by the value of $RA_{n,i}$, which is a direct function of the slope of the equilibrium curve. For a system with a relatively flat equilibrium curve the value of $RA_{n,i}$ will be very small and $\frac{RA_{n,i}}{NL_{n,i}}$ can be ignored giving a gas film controlled system. A liquid film controlling system is obtained for the systems with a steep equilibrium curve.

For the formaldehyde-hemiformal-methanol-methylene glycol-water system no simplifying assumption should be made, as the slope of the equilibrium curve is considerably different for each of the components and therefore both terms should be considered.

4.4.3 Efficiency of the Reboiler Stage

The form of equation known as the vaporisation efficiency is obtained by application of the Murphree efficiency to the reboiler stage. The value of Y_{n-1} in equation 4.60 will be zero as no vapour is entering the boiler. Unless some experimental vaporisation efficiency values are available, the application of this efficiency definition will result in the further problem of evaluating the vaporisation efficiency. It was therefore decided to apply a new definition of efficiency for the

boiler stage by replacing the Y_{n-1} in equation 4.60 with X_{n-1} . The resulting relationship is in the form of equation 4.82. The values of the efficiency are evaluated by trial and error procedure. The value was found to be 0.4 for all the experiments and therefore an accurate and convenient method of evaluation of efficiency was obtained

$$E_b = \frac{Y_1 - X_1}{Y_1^* - X_1} \quad (4.82)$$

CHAPTER 5

DESCRIPTION OF COMPUTER PROGRAMS

5. DESCRIPTION OF COMPUTER PROGRAMS

5.1 INTRODUCTION

The solution of the mathematical models developed in Chapters 3 and 4 and the associated computer programs are discussed in this chapter. The numerical techniques were applied to the relationships representing the vapour-liquid equilibrium, the distillation calculations and the chemical reaction equations and a series of computer programs were obtained which represent the steady state mathematical model for the distillation of formaldehyde solutions.

Four types of computer programs can be generally formulated. Firstly, auxiliary programs are used to process the data to be employed in the modelling programs. Processing the experimental data into quinary format, estimating the constants for the correlation of vapour pressures from the experimental data and generating vapour pressure data for the components whose vapour pressures are not reported in the literature from the vapour and liquid mole fractions can be cited as examples of auxiliary programs.

Secondly, parameter estimation programs were used to estimate constants in equations such as those defining the liquid phase activity coefficients. Several methods of optimisation were tried for this program and these have been explained in Chapter 3: Marquardt's method was

found to be more suitable. In this section, only the programs with Maquardt's method of optimisation will be explained, since this method was used for the modelling calculations.

Thirdly, the vapour-liquid equilibrium calculations for the reacting systems were executed using the bubble point method in the form of computer programs. The estimated parameters and the data obtained from the auxiliary programs, combined with the data reported in the literature were used for these programs. These programs were based on the theory explained in Chapter 3 for the vapour-liquid equilibrium of the chemically reacting systems.

Fourthly, the distillation column calculations were combined with the vapour-liquid equilibrium programs to solve the mathematical models which had been developed for the formaldehyde-methanol-water system.

In this chapter the above programs have been categorised into three sections i.e. the vapour-liquid equilibrium programs, the parameter estimation programs and programs for the distillation column.

An attempt has been made to construct the computer programs in a general form so that these could be applied to any reacting system containing any number of components, with minimum modification. In order to simplify the

approach to the programming, each section of the calculations was assigned to a different subroutine, separating the calculations into various stages.

A central MASTER segment is contained in each program coordinating the subroutines and controlling the interaction of the different subroutines. Some of the MASTER segments in the type three programs may be used as a subroutine in the type four programs. Necessary modifications had to be carried out in these segments in order to make them compatible with the remaining subroutines.

The Honeywell 316 Computer in the Department of Chemical Engineering, the Aston University Computer, an ICL 1904S and Manchester University regional computer, which is a hybrid of a CDC 7600 and ICL 1904S, were used as the computing facilities in this work.

The first type or the auxiliary programs were executed on the Honeywell 316 Computer using BASIC language. The types two, three and four programs were first filed in the ICL 1904S Computer for any necessary corrections and developing. After the programs had been corrected, the programs were transferred to the much larger and faster computer of CDC 7600 and ICL 1904S for the main calculations and results.

5.2 VAPOUR-LIQUID EQUILIBRIUM PROGRAMS

The variables and relating equations in a vapour-liquid equilibrium system, where the components of the system exist in a chemical equilibrium, have been discussed in Chapter 3. The thermodynamic properties of the system in phase equilibria are specified when m independent variables are given, where m is the number of components. However, a larger number of quantities are normally required, in particular, the pressure, temperature, m liquid phase mole fractions and m vapour phase mole fractions. In the case of chemically reacting systems, extra variables have to be evaluated whilst for systems with no chemical reaction, $2m+2$ variables are found to exist. For the formaldehyde-methanol-water system, four extra variables are introduced and these are the number of moles reacted in two different reactions in two different phases. Thus the number of variables is increased to $2m+6$. The $m+1$ independent variables are specified for the system by the given mole fraction of a phase and pressure or temperature. The number of unknown variables is $m+5$ and these can be determined by the solution of m equilibrium relationships, one stoichiometric relationship and four chemical reaction relationships.

An efficient solution of these complex equations can be based on appropriate mathematical techniques which exploit the high speed of digital computers. The computer

programs for the solution of the above equations are explained in this section.

In this work the program was applied only for the bubble temperature calculations because this type of calculation was observed to be more suitable for molar distillation calculations. The iteration variables have to be modified for dewpoint calculations.

The vapour phase mole fractions and the equilibrium temperature are evaluated in the bubble temperature calculation, knowing the liquid mole fraction and the pressure.

The phase equilibria is defined by the equality of fugacities in phases for each of the components as explained in Chapter 3. The stoichiometric relationship is defined by equations 5.1 and 5.2.

$$\sum_{i=1}^m X_i = 1 \quad (5.1)$$

$$\sum_{i=1}^m Y_i = 1 \quad (5.2)$$

The chemical equilibria equations are defined by equations 5.3 to 5.6.

$$K_1^V = \frac{P \cdot Y_5 \cdot Y_1}{Y_4} \quad (5.3)$$

$$K_2^V = \frac{P \cdot Y_3 \cdot Y_1}{Y_2} \quad (5.4)$$

$$K_1^L = \frac{X_1}{X_4} \quad (5.5)$$

$$K_2^L = \frac{X_2}{X_3 X_1} \quad (5.6)$$

The activity coefficients, the liquid partial molar volume and the vapour phase fugacity coefficients were used in the above equations. These quantities were calculated using the thermodynamic relationships given in Chapter 3. Calculation of these quantities are performed in different subroutines which are described in the following sections. The subroutines RSTATE, ACTCO, PHIMIX, VIRIAL, INPUT, OUTPUT and program VAPFIT are based on programs developed by Prausnitz, Eckert, Orye and O'Connell (191).

5.2.1 Subroutine RSTATE

Subroutine RSTATE is used to calculate the liquid reference state fugacity and the partial molar volume of each of the components in the mixture. The fugacity of the saturated liquid corrected to zero pressure and the pure component liquid molar volume, both of which are functions of temperature only, are calculated for subcritical components in this subroutine. For a subcritical component, the pure liquid molar volume is an approximation to the partial molar volume to correct the pure component fugacity to the system pressure. The pure liquid molar volume is also used in the calculation of activity coefficients with the Wilson equation. In

an isothermal calculation, RSTATE has to be called once, whilst in an isobaric calculation RSTATE must be recalled for each new estimate of the temperature.

Two different thermodynamic approaches are being used for condensable and noncondensable components. The condensable components are those whose critical temperatures are below or only slightly above the temperature of the mixture. In this case, the symmetric convention is used for the activity coefficients. The noncondensable components are further above their critical temperatures and the unsymmetric convention is used. For a noncondensable component, Henry's constant for the component in a chosen reference solvent is used as the reference fugacity, whilst the partial molar volume in a multicomponent mixture is a function of the experimental binary partial molar volumes at infinite dilution.

Because the critical temperatures of hemiformal, methanol, methylene glycol and water are all above the usual range of the system temperature, these components were all treated as condensable components. However, formaldehyde has been treated as a supercritical component.

The subroutine is started with DIMENSION and COMMON statements where all the communication with this subroutine is carried out through the COMMON statements.

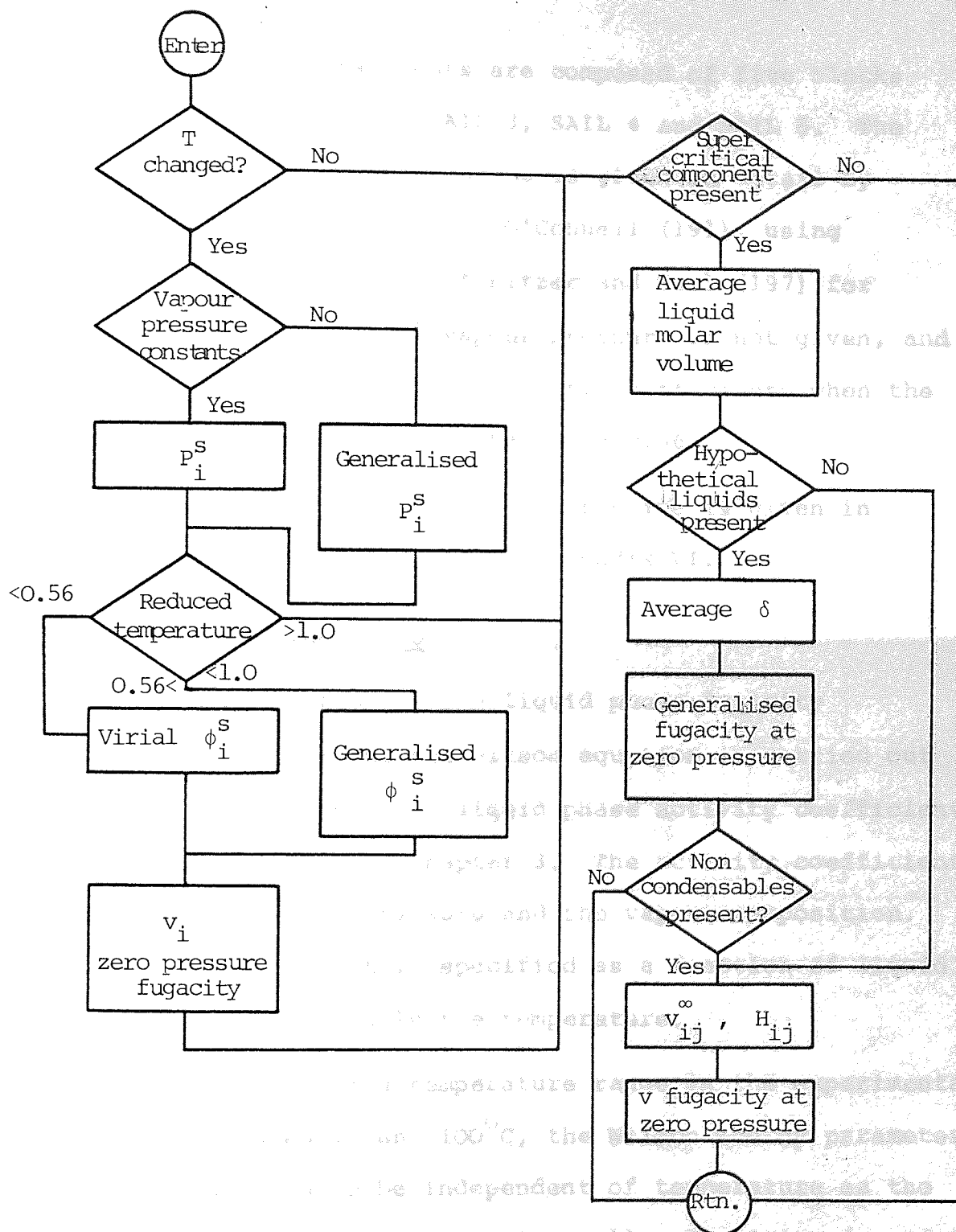


Figure 5.1 flow diagram of subroutine
RSTATE

The COMMON statements are composed of five blocks namely SAIL 1, SAIL 2, SAIL 3, SAIL 4 and SAIL 5. The description of this subroutine is given in detail by Prausnitz, Eckert, Orye and O'Connell (191), using the generalised methods of Pitzer and Curl (197) for vapour pressure, if the vapour pressure is not given, and Lyckman et al (242) for fugacity coefficients when the reduced temperature is greater than 0.56.

The flow diagram of this subroutine is given in Figure 5.1 and the listing in Appendix VI.

5.2.2 Subroutine ACTCO

The calculation of the liquid phase activity coefficient utilising the Wilson equation is carried out in this subroutine. The liquid phase activity coefficient has been explained in Chapter 3. The activity coefficient is not affected by pressure and the vapour composition. Thus the coefficient is specified as a function of liquid composition and usually the temperature.

As the operating temperature range in the experimental work was between 70 and 100°C, the Wilson energy parameter could be assumed to be independent of temperature as the variation in the temperature is small. Provision is made in this subroutine for the calculation of activity coefficients in both the symmetric and unsymmetric conventions.

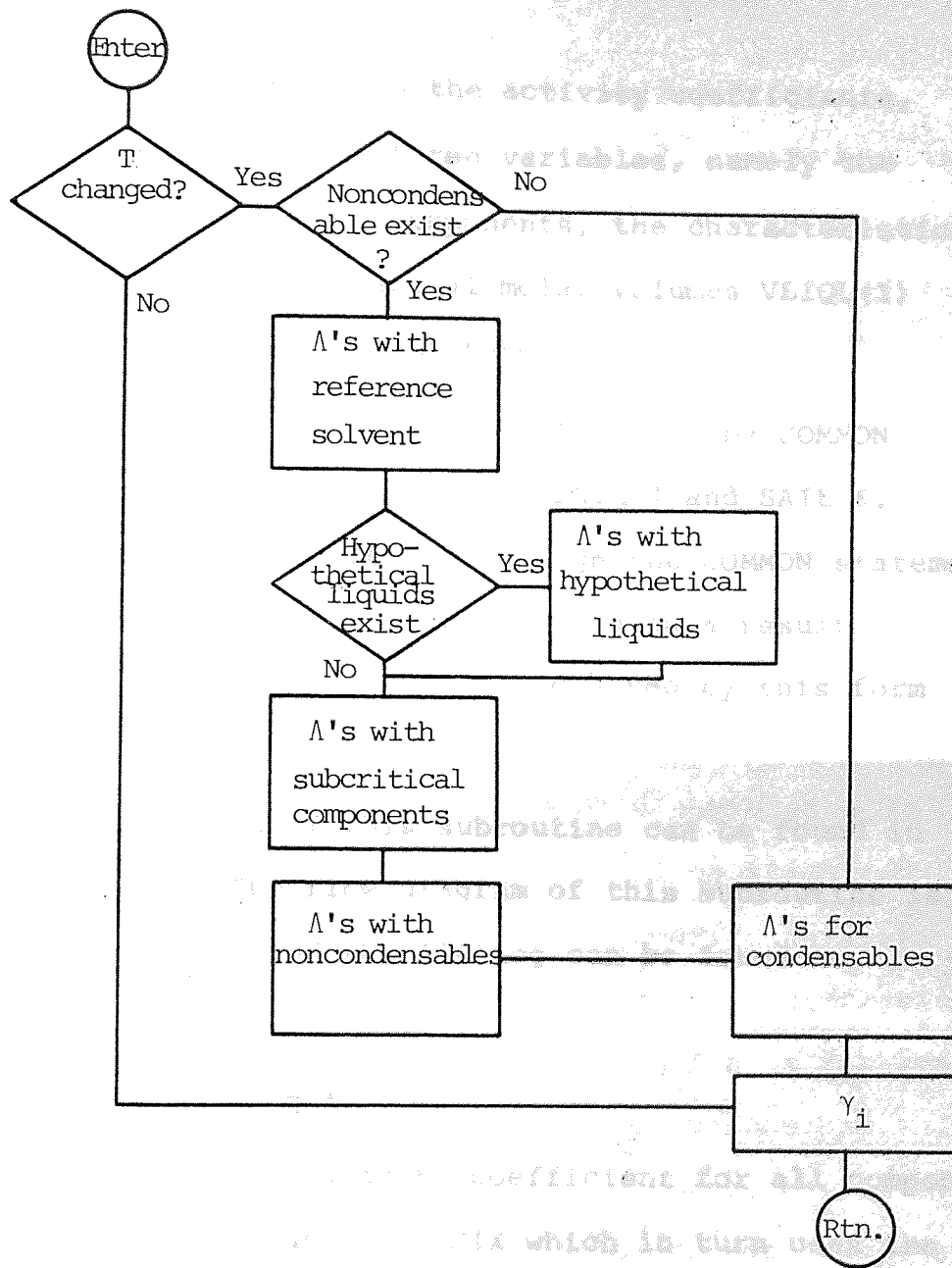


Figure 5.2. Flow diagram of subroutine

ACTCO

In the Wilson equation the activity coefficients, $\text{GAMMA}(I)$, are governed by three variables, namely the liquid composition of all components, the characteristic molar volume $\text{VLIQ}(I)$ or partial molar volumes $\text{VLIQL}(I)$ and the temperature of the mixture T .

The DIMENSION statements were followed by COMMON statements SAIL 1, SAIL 2, SAIL 3, SAIL 4 and SAIL 6. The information is transferred through the COMMON statements because of the large volume of data and as a result considerable computation time can be saved by this form of communication.

The description of this subroutine can be found in reference (191). The flow diagram of this subroutine is given in Figure 5.2 and the listing can be found in Appendix VI.

5.2.3 Subroutine PHIMIX

The vapour phase fugacity coefficient for all components is evaluated in subroutine PHIMIX which in turn uses the equation of state for the vapour phase. The fugacity coefficient is defined in terms of both temperature and pressure as well as vapour composition. Thus the calculation must be repeated for every change of any of these variables. However, very small changes in the fugacity coefficient are caused by relatively large changes of temperature, pressure and composition which is desirable for efficient convergence scheme.

The virial equation of state is used for the calculation as explained in Chapter 3. The second virial coefficient must be calculated first in order to calculate the vapour phase fugacity coefficient. The second virial coefficients are calculated in a different subroutine which is explained in Section 5.2.4.

In the course of using the volume series virial equation to calculate the fugacity coefficient, the vapour phase molar volume must be evaluated by solving a quadratic equation. This equation under certain conditions has only imaginary roots. This situation is reached when the temperature and pressure of the gas have approached a critical value. The volume series virial equation can still be used when higher order virial coefficients are introduced. The conditions which lead to this difficulty are usually found to occur when the iteration is far away from the actual solution. Some numerical values are required so that the program can make a better choice on the next iteration. Furthermore, the major nonidealities are generally found in the liquid phase and not in the vapour phase. Thus although errors are obtained in the vapour calculations, much smaller errors are obtained in the calculated equilibrium conditions.

Thus when the preferred volume series form does not possess real roots, the pressure series virial equation is used. A real root can always be obtained from this

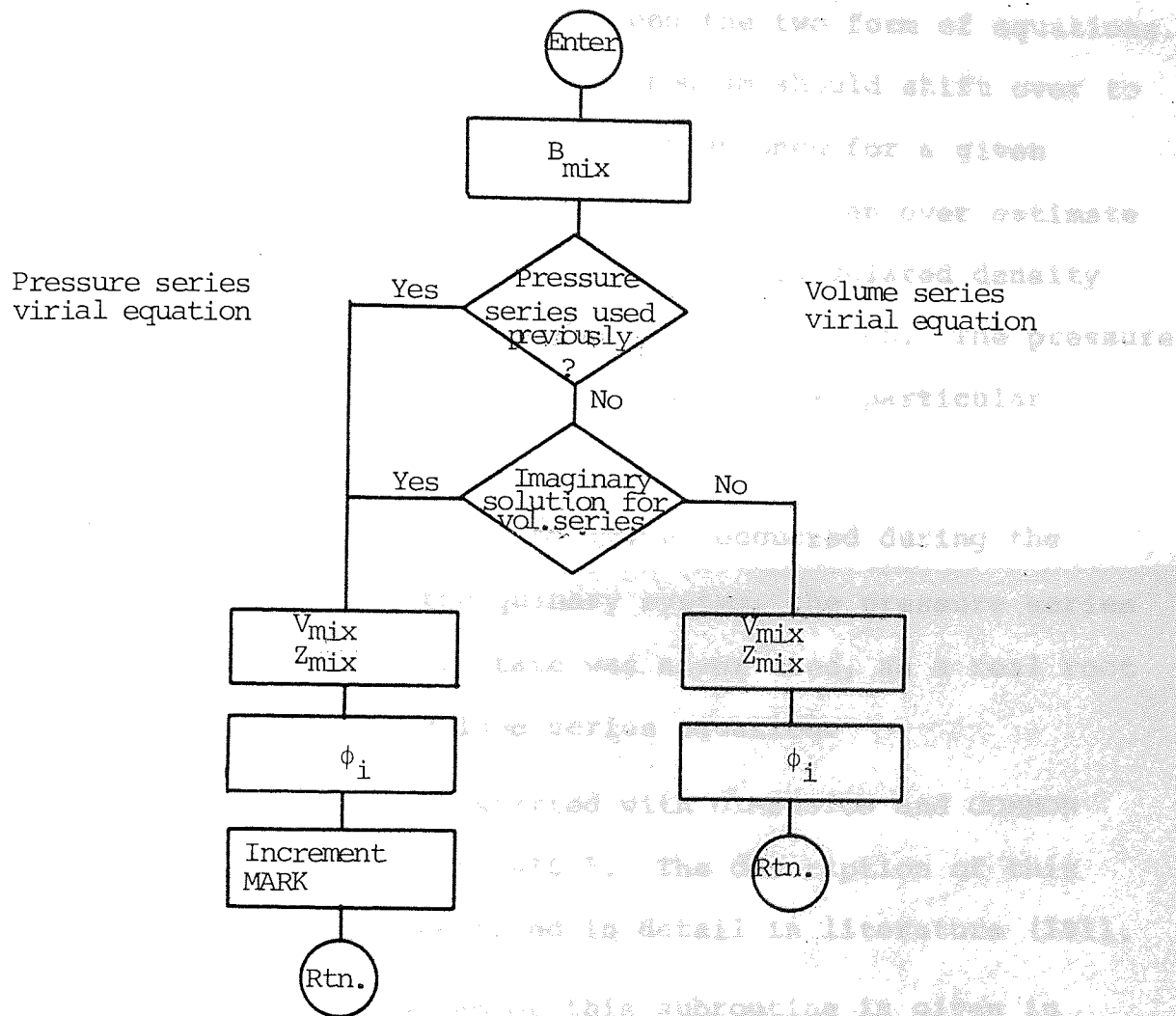


Figure 5.3. flow diagram of subroutine

PHIMIX

form of equation of state for the volume. A problem of discontinuity in the calculated results may be introduced by the shift between the two form of equations. It is specified that if the program should shift over to the pressure series form more than once for a given calculation, it is then not the case of an over estimate of pressure but it is one where the calculated density is too large for the volume series equation. The pressure series is then used for the rest of that particular calculation.

Although extreme conditions occurred during the calculations for the quinary system, the pressure series form of equation of state was never used, as a real root was given by the volume series equation.

The program is started with DIMENSION and COMMON statements SAIL 1 to SAIL 5. The description of this subroutine could be found in detail in literature (191).

The flow diagram of this subroutine is given in Figure 5.3 and the program listing can be found in Appendix VI.

5.2.4 Subroutine VIRIAL

This subroutine is used as a support program for subroutine PHIMIX which employs the virial equation. The virial coefficients for all possible pairs of pure components are calculated as a function of temperature

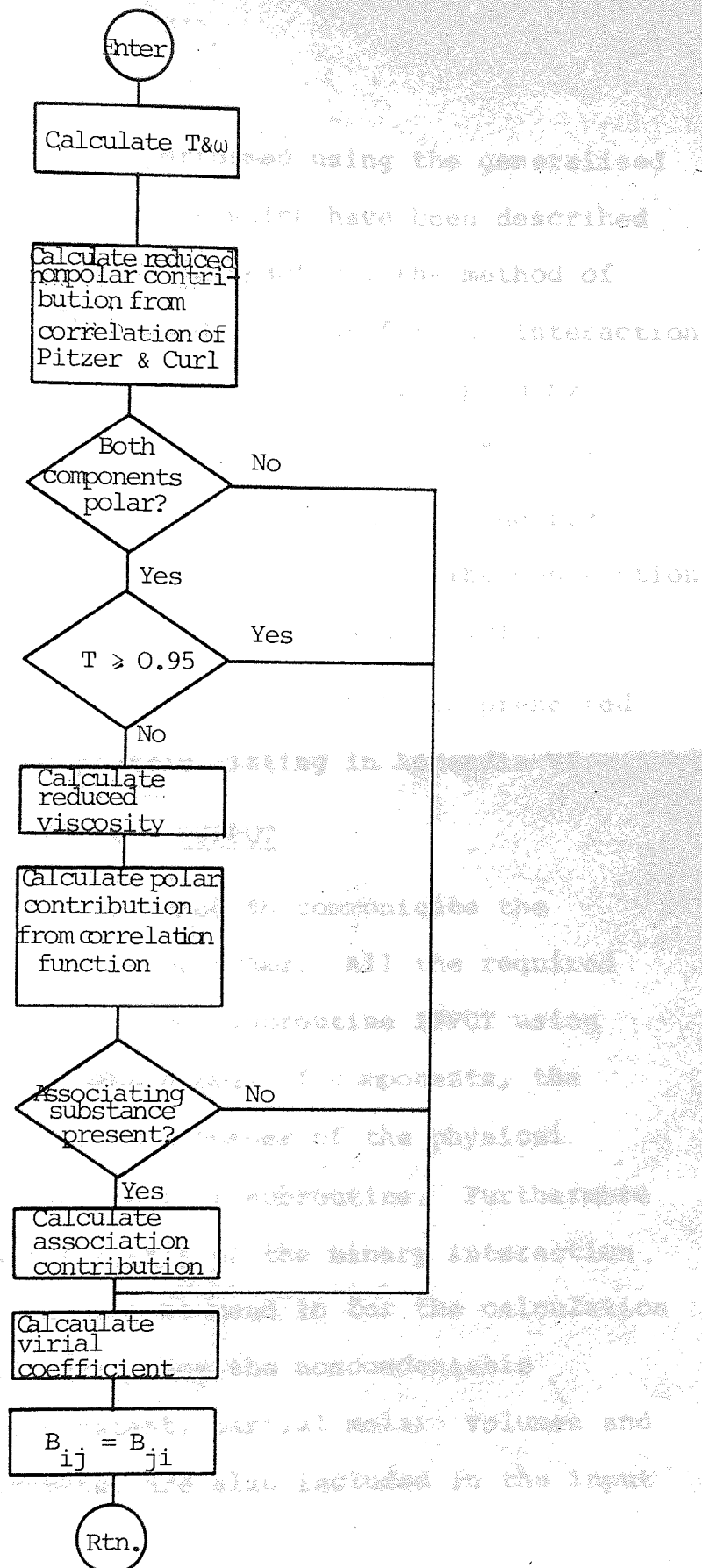


Figure 5.4 — flow diagram of subroutine
VIRIAL

only. The calculation is performed using the generalised corresponding state techniques which have been described in Chapter 3. For nonpolar interaction, the method of Pitzer and Curl (197) was used, whereas for the interaction involving polar species the correlation presented by Prausnitz, Eckert, Orye and O'Connell (191) was used.

The subroutine is started with DIMENSION and five COMMON statements namely SAIL 1 to SAIL 5. The description of the program could be found in literature (191).

The flow diagram of subroutine VIRIAL is presented in Figure 5.4 and the program listing in Appendix VI.

5.2.5 Subroutines INPUT and OUTPUT

These subroutines are used to communicate the information to or from the programs. All the required parameters are read in through subroutine INPUT using standardised formats. The number of components, the name of each component and a number of the physical properties are included in this subroutine. Furthermore the parameters characteristic of the binary interaction of the liquid mixture must be read in for the calculation of activity coefficients. For the noncondensable components, Henry's constant, partial molar volumes and Wilson's single parameter are also included in the input data.

Subroutine INPUT is called only once for the calculations,

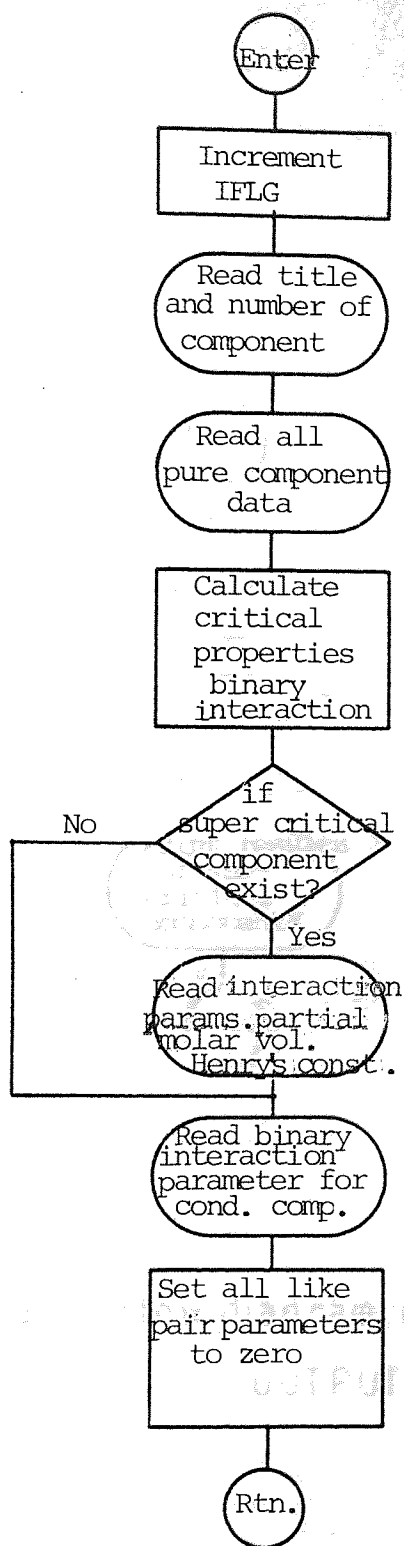


Figure 5.5 flow diagram of subroutine

INPUT

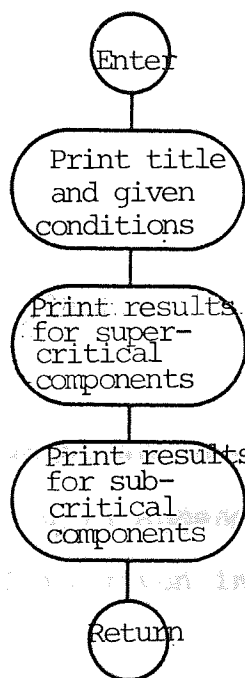


Figure 5.6 flow diagram of subroutine OUTPUT

since there would be no change in the components of the system. The independent variables, pressure and liquid mole fractions are read in by the main program and not by this subroutine.

Subroutine OUTPUT is called when a convergent solution has been achieved for each calculation and the subroutine is used to print out all the desired results.

The description of both subroutines and the data formats are given by Prausnitz, Eckert, Orye and O'Connell (191).

The flow diagram of subroutine INPUT is given in Figure 5.5 and listing in Appendix VI. The flow diagram of subroutine OUTPUT is given in Figure 5.6 and listing in Appendix VI.

5.2.6 Subroutine MODCON

This subroutine is developed for the calculation of vapour phase compositions at chemical equilibrium. The equations which are used in this subroutine have been explained in Appendix I, using the results from Appendix III. The subroutine is used to modify the calculated values of vapour phase mole fractions from the thermodynamic relationships. The calculated values of vapour mole fractions from this subroutine are a function of pressure and temperature.

The subroutine is started with the arguments Y,P and

T in the call statement, where these are used to communicate the information to and from this subroutine. The value of Y is set to the vapour phase mole fractions which is not at chemical equilibrium. These values are applied to the relationships defining the vapour phase chemical reaction and the new values are stored in the same location. The current pressure and temperature values are contained in the variables P and T.

After the DIMENSION statement, two mathematical function statements are used to define the vapour phase chemical reaction constants as a function of temperature.

The coefficients of the cubic equation defining the number of reacted moles for the hydration of formaldehyde are calculated according to equation I.11 at statement 10. The Newton-Raphson method is used to solve the cubic equation using an initial guess of zero for the variable. The value of the derivative of the function is calculated and used for the iterative solution. If convergence is not achieved in three hundred iterations, the program is halted and a message is printed out to inform that convergence has not been achieved. If convergence is reached within the set limit, the program is transferred to statement 20 where the values of the vapour phase mole fractions in chemical equilibrium are calculated and stored in location Y. The program is transferred by the RETURN statement to the call statement for this subroutine.

The flow diagram of this subroutine is given in

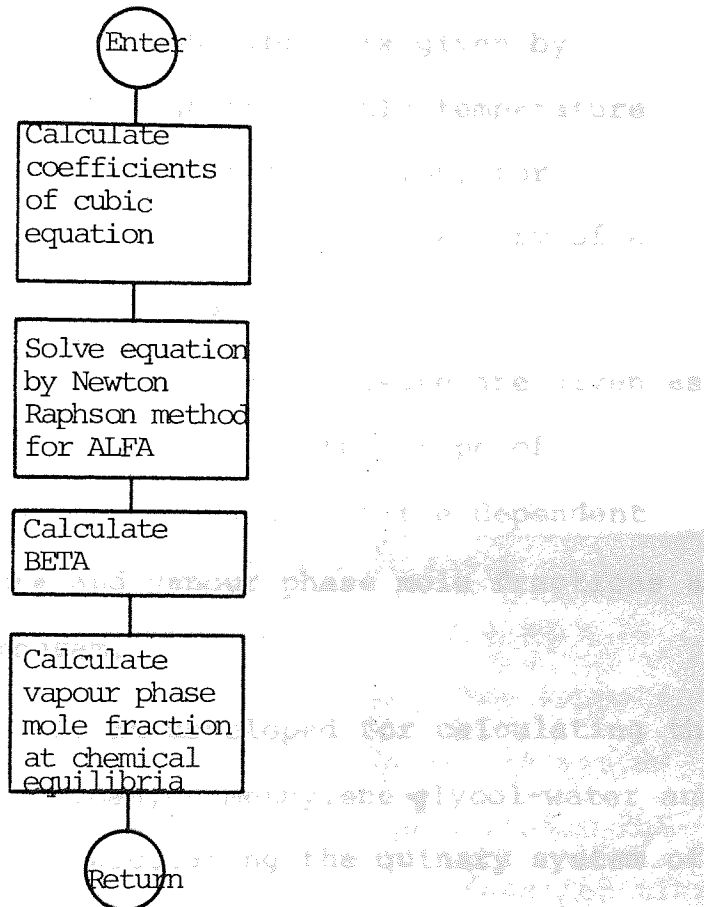


Figure 5.7 flow diagram of subroutine
MODCON

Figure 5.7 and the listing in Appendix VI.

5.2.7 Subroutine BUBLDILF

The main segment for the calculation of multicomponent vapour-liquid and chemical equilibria is given by subroutine BUBLDILF. Although the bubble temperature calculations are calculated in this section, for convenience the section is developed in the form of a subroutine and not a MASTER segment.

The liquid mole fractions and pressure are given as the independent known variables for this type of calculation. The equilibrium values of the dependent variables, temperature and vapour phase mole fractions are calculated by the program.

This program was first developed for calculating the ternary system of formaldehyde-methylene glycol-water and later was extended for calculating the quinary system of formaldehyde-hemiformal-methanol-methylene glycol-water. However only the extended version of the program will be discussed here because this is a general program and can be applied to the ternary system as well as the quinary system. The program for the quinary system can be applied to the ternary system by setting the liquid phase mole fractions of hemiformal and methanol to zero.

The calculations are based on the solution of m equilibrium equations, the stoichiometric relationships, equation 5.2 and two vapour phase chemical equilibrium

relationships 5.3 and 5.4. Due to the nature of the program it is believed that the calculations are more sensitive to temperature than to the vapour composition. Therefore, the solution of the simultaneous equations is achieved by first choosing a temperature and by an iterative method in which the vapour phase mole fractions are calculated at that temperature. The vapour phase composition is then modified to allow for a chemical reaction in the vapour phase. The system pressure is calculated using the vapour phase mole fractions. The calculation is iterated until no change is obtained in the calculated total pressure. The difference of the calculated pressure with the given system pressure is used for making successive re-estimates of the temperature until the difference between the calculated and system pressure is negligible and the problem is solved. The number of calculations and the required computation time are minimised by using this technique.

The required data are read in by the main segment and subroutine INPUT. An initial guess for temperature is also read in by the MASTER segment for the calculation of the first set of data. The temperature calculated for the first set of data is used as an initial estimate for the second set of data and this procedure is carried out for all the other sets of data. The vapour phase fugacity coefficients are set equal to unity for the first iteration.

The calculations are started by utilising the known values together with the pressure and liquid compositions which are combined with the guessed value of the temperature. The virial coefficients B_{ij} in subroutine VIRIAL, the liquid molar volume and reference state fugacity in subroutine RSTATE and the liquid activity coefficients in subroutine ACTCO are found by these calculations. These results are applied to equation 3.49 for the calculation of fugacities of the phases.

Once the fugacities at temperature T have been calculated, the inner iterative loop is entered for the calculation of the vapour phase composition. For the first iteration, the fugacity coefficients have been set at unity and the vapour mole fractions are found from equation 5.7.

$$Y_i = \frac{f_i}{P} \quad (5.7)$$

The values of Y_i are modified in subroutine MODCON. The partial pressures are calculated and summed over the components to calculate the system pressure, which is a decisive variable in the iteration. The calculated values of the vapour phase composition are used to evaluate the fugacity coefficients, which may be used to improve the vapour composition estimates. The resulting new value of the system pressure is compared with the previous value to determine if any change has taken place.

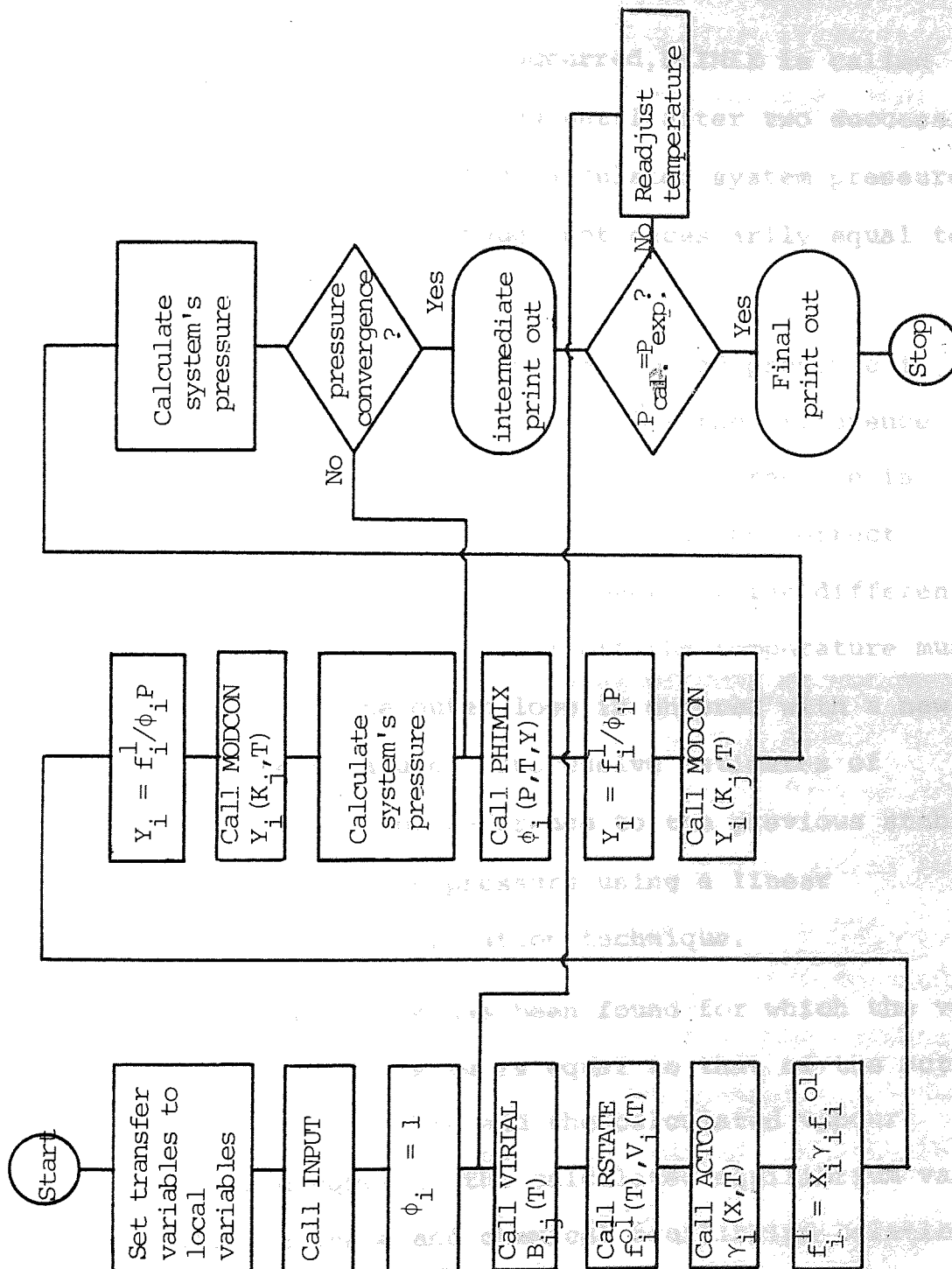


Figure 5.8 flow diagram of subroutine BUBLDILF

If a significant change has occurred, PHIMIX is called and the procedure is continued until after two successive iterations the value of the calculated system pressure has remained constant although not necessarily equal to the actual system pressure.

The constant value of the calculated pressure is compared with the actual pressure. If the difference between the calculated and actual system pressure is found to be within the tolerance limit, the correct temperature has been chosen. However, if the difference is greater than the tolerance limit the temperature must be readjusted and the outer loop is entered with a new value of the temperature. Successive estimates of temperature are made by reference to the previous stable value of the calculated pressure using a linear interpolation and extrapolation technique.

When a temperature has been found for which the value of the calculated pressure is equal to that of the actual pressure, the temperature and the calculated vapour composition are equal to the calculated equilibrium values because all the phase and chemical equilibrium relationships have been satisfied. Then subroutine OUTPUT is called to print the calculated values.

The arguments X, Y, T and P in the call statement are used to start the program in order to transfer the given and calculated values from this subroutine. The

call statement is followed by the DIMENSION statements and COMMON block FLEET is used to communicate a flag, IFLG, between subroutine BUBLDILF and INPUT, so that the subroutine INPUT can be entered only once at the start of the calculations. All the variables which need to be transferred to or from the subroutines are placed in the COMMON storage. The calling sequence of the subroutines are simplified by this procedure and a saving is made on computer time and storage locations.

The calculations are started with the translation of the variables in the calling sequence to the local variables in DO 12 loop. The value of SUMX is set to unity where SUMX is used as a normalisation factor in ACTCO.

The value of IFLG is checked and if this value is zero the subroutine INPUT is called to read in the pure component data and the value of IFLG is increased by one. If the value of IFLG is positive, the calculation is transferred by the IF statement to statement 509 so that the calculations may be continued and the CALL INPUT statement is avoided.

The vapour phase fugacity coefficients are initialised in DO 510 loop where these values are set at unity. On the first iteration the perfect gas approximation is used as the starting point for the calculations. In the following iterations the value of PHI is updated by

calling subroutine PHIMIX. One are made for the composition

The IF statement after the DO loop is used as a flag to communicate to the programs that a different system is to be calculated, if that is the case. The calculations are returned by a negative value of P to the main segment without proceeding with any calculations. The calculations are sent by a zero value of P to CALL INPUT statement. The program is made to proceed with the calculations at statement 530 by a positive or actual value of P. The value of the previous temperature is set to zero by this statement for the first iteration. The print out of the headings for the intermediate print out of the lap by lap results are caused by the two following WRITE statements.

The outer iteration loop for temperature is entered at statement 540 where RT is calculated. The lap counting variable for the inner iteration of vapour composition and pressure, KOUNT, is set at zero and subroutines VIRIAL, RSTATE and ACTCO are called. These subroutines are called in a particular sequence because RSTATE may use some of the virial coefficients calculated in VIRIAL, and the Wilson equation in ACTCO uses the temperature dependent liquid molar volumes calculated in RSTATE.

The quantity TOLD is used as a storage location for the temperature at which the subroutines ACTCO and RSTATE were called.

The initial calculations are made for the fugacities, the vapour compositions and SUMY in the DO 550 loop. The subroutine MODCON is called to evaluate the composition of the vapour phase at chemical equilibrium. The value of SUMY is recalculated at DO 551 loop.

The system pressure is calculated at DO 555 loop and is stored in location PINT. The location PINTO is used to store the old values of PINT and the variable MARK is set at minus one. This variable is used to communicate the type of virial equation which is utilised in subroutine PHIMIX.

The inner loop for the calculation of the vapour phase composition is entered at statement 560. The molar vapour volume VMIX is checked after calling PHIMIX. A negative VMIX value would be obtained if the input pressure was set too high in the virial equation. As a negative value of VMIX cannot be interpreted realistically and also because further disruption would be caused in the program, the calculations are transferred to the OUTPUT subroutine and further calculation is avoided for this particular set of data.

After the IF statement the lap counter, KOUNT, is increased by one and a new value for the vapour phase composition is calculated in DO 570 loop, followed by the SUMY value. The values of the vapour phase compositions are modified according to the vapour phase chemical reaction

relationships in subroutine MODCON.

The system pressure is calculated in DO 575 loop and stored in PINT. The value of PINT is compared with the previously obtained value stored in PINTO to determine whether PINT is constant within the permitted tolerance. If PINT has not converged on a constant value, the program is directed to statement 580 where PINT is stored in PINTO and the calculation is transferred to statement 560, the beginning of the inner loop.

When a constant value of PINT is achieved, the program has calculated the equilibrium values of the vapour phase composition and temperature T at pressure PINT. If PINT is equal to the system pressure, T is denoted as the thermodynamic equilibrium temperature. If PINT is not equal to the system pressure, T must be adjusted until PINT is equal to the actual system pressure. When the constant value of PINT is found, the program is transferred to statement 590 where the difference between PINT and the actual system pressure P is stored in PINT1. This step is followed by an intermediate WRITE statement in which the lap to lap progress of the program towards convergence is shown. When the calculated pressure is equal to the system pressure i.e. at PINT1 equal to zero, the program is transferred directly to subroutine OUTPUT at statement 650.

However, the temperature must be adjusted if the

difference is found to be greater than the permitted tolerance limit.

In the first lap a different adjustment procedure for the temperature must be used because a previous value is required by the linear procedure for comparison. The temperature of the previous iteration TPREV is checked by statement 595 and TPREV is set to zero for the first iteration. In the first iteration, the current value of the temperature is stored in TPREV for use in the next iteration. In this iteration the temperature is adjusted according to the sign of PINT1. If PINT is greater than P, the value of the current temperature being used has been determined to be higher than the actual value. If PINT is less than P, the value of the current temperature being used has been determined to be lower than the actual temperature. On this basis, the temperature is incremented by 2 percent in the direction determined by the sign of PINT1 through statement 605 to 610.

In systems where noncondensable components are present, the above mentioned temperature prediction procedure may not be true but convergence of the program is not prevented by this problem. However, a larger calculation time may be required to achieve convergence. After the increment in the temperature, the program is transferred to statement 540 to start the outer loop iteration with the new temperature.

After the initial iteration, a positive value is located in TPREV and the program is transferred by statement 595 to the linear interpolation scheme to adjust the temperature starting with statement 615. The variable slope is found as the ratio of the change in temperature to the change in PINT, where PINT is stored in PINTP and T is stored in TPREV. The DELT, the change in temperature, is found as the product of the multiplication of SLOPE by PINT1. A limit is imposed on the magnitude of DELT to prevent large changes in temperature. The magnitude of the increment is lowered in statement 620 if the change in temperature exceeds 10 percent of T and the program is returned to statement 540.

All equations of the phase and chemical equilibria are satisfied when the program has arrived at a value of PINT which is both stable and equal to P and the program is transferred to the OUTPUT subroutine through statement 650. After the final results have been printed by OUTPUT, MARK is checked to find if any irregularities have occurred in the vapour phase calculations. Any vapour phase irregularities are indicated by a WRITE statement 655.

Finally the calculated values of Y and T which are local variables, are put equal to the transfer variables in DO 652 loop and the program is returned to the main segment through a RETURN statement.

The flow diagram of this subroutine is presented in Figure 5.8 and a listing is given in Appendix VI.

5.2.8 Master Segment for Vapour-Liquid Equilibrium Calculations, SD

The master segment for the calculation of the vapour-liquid equilibrium is only used for reading the liquid phase compositions which are in chemical equilibrium, the system pressure, the number of data points and initialising the flag for subroutine INPUT.

The program is started with the DIMENSION and COMMON statement FLEET, containing the flag IFLG. The number of data points and the initial guess for the temperature are read as the first stage of the calculation. The liquid phase mole fractions are read in DO 100 loop and the value of IFLG is set at zero. The mole fractions of the liquid phase are stored as transfer variables in DO 110 loop and subroutine BUBLDILF is called. After DO 110 loop is completed, the calculation is stopped with the STOP statement.

The flow diagram of this segment is given in Figure 5.9 and listing in Appendix VI.

5.3 PARAMETER ESTIMATION

A number of pure component properties are required for the phase equilibria calculations in different programs.

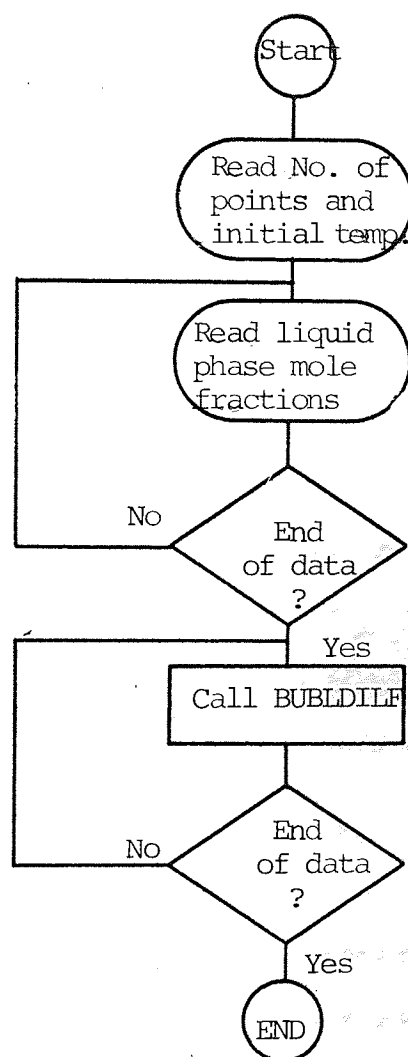


Figure 5.9 flow diagram of program

SD

The pure component information which is required by these programs is as follows: (1) the critical properties used for the estimation of the vapour phase nonidealities, (2) liquid molar volumes at one or preferably three temperatures which cover the major portion of the liquid range, (3) vapour pressure constants for the generalised equation which defines the temperature dependence of vapour pressure of a pure component, (4) the definition of the enthalpy of a pure component as a function of temperature and (5) the heat of vaporisation, as a function of temperature. The parameters in groups 4 and 5 are used only in the distillation column calculations but the parameters in groups 1, 2 and 3 are used in all the programs. The value of these parameters and the method of their estimation is presented in Appendix V.

In order to calculate the non-ideal behaviour in the vapour phase, at least one parameter for the nonpolar components and upto four parameters for polar components which exhibit molecular association, have to be evaluated. The use of these parameters in the virial equation of state has been discussed in Chapter 3. The four parameters for polar components are, (1) the acentric factor which may be determined from the pure component vapour pressure at a reduced temperature of 0.7, (2) the acentric factor of the homomorph of a polar component, (3) the dipole moment for polar species and (4) an empirical association constant used to correlate experimental data for the

virial coefficients of polar gases which may form hydrogen bonds.

In the programs the liquid molar volume of a component at any temperature T may be calculated from equation 5.8. The constants in this equation are calculated from equations 5.9-11 provided three data points are available.

$$V^L = a + bT + cT^2 \quad (5.8)$$

$$c = \frac{(T_3 - T_1)(V_2^L - V_1^L) - (V_3^L - V_1^L)(T_2 - T_1)}{(T_2^2 - T_1^2)(T_3 - T_1) - (T_3^2 - T_1^2)(T_2 - T_1)} \quad (5.9)$$

$$b = \frac{(V_2^L - V_1^L) - c(T_2^2 - T_1^2)}{T_2 - T_1} \quad (5.10)$$

$$a = V_1^L - bT_1 - cT_1^2 \quad (5.11)$$

The values T_1 , T_2 and T_3 are the temperatures at which the pure component liquid molar volumes V_1^L , V_2^L and V_3^L are given.

A linear interpolation scheme is provided by equations 5.12-14 if the liquid molar volume is available at only two temperatures.

$$c = 0 \quad (5.12)$$

$$b = \frac{V_2^L - V_1^L}{T_2 - T_1} \quad (5.13)$$

$$a = V_1^L - bT_1 \quad (5.14)$$

Accurate values of these data however could not be found in the literature for components such as formaldehyde, hemiformal and methylene glycol. Therefore, these properties had to be evaluated employing the general techniques for the estimation of physical properties. The accuracy of these methods does not exceed the accuracy of the experimental data.

Provision has been made in subroutine INPUT for the reading of the constants of the six parameter vapour pressure relationship in the form of equation V.6. This form of the equation can be reduced to many of the equations which are presented in the literature.

A program to determine the constants of the vapour pressure equation has been written (191) where the constants are calculated from the vapour pressure data at different temperatures.

Two Wilson parameters must be specified for each binary pair of condensable components in a multicomponent system. These parameters are subsequently used by subroutine ACTCO for the calculation of the activity coefficients of each species in the solution. The non-condensable components are specified by Henry's constant and the Wilson single parameter. These parameters have been explained in Chapter 3. A program, COMP5, was developed for the estimation of the binary parameters and Henry's constant.

5.3.1 Program VAPFIT

This program is only explained briefly as the full explanation can be found in the literature (191).

This program is used to estimate the constants for equation V.6. The acentric factor and the liquid molar volumes at different temperatures are calculated in this program. The critical pressure, critical temperature, molecular weight, liquid densities and vapour pressure at different temperatures are required as input data by VAPFIT.

The vapour pressure data are fitted to the general form of equation V.6 in terms of the constants CPSAT1 to CPSAT6. The best set of constants for each pure component are found for this equation by a linearisation and trial and error procedure. The linearised form of the equation is presented by equation 5.15.

$$(\ln P - C_6 \ln T)T = C_2 + C_1 T + C_4 T^2 \quad (5.15)$$

A value is assumed for C_6 and then the optimum values for ^{the} remaining three parameters may be found by a least squares matrix inversion method. Successive iterations are made for different estimates of C_6 until the set of four constants are found which minimise the percentage difference between the data and the calculated values of the vapour pressure.

The maximum number of laps for changes made to CPSAT(6) is set at fifty and the minimum incremental variation applied to CPSAT(6) is restricted by DCPMIN to 1×10^{-5} .

The pure component data are first read by the program and then the identification headings are read in followed by the number of data points, the critical properties, the molecular weights and the desired percent error ERRMAX. The name of pure component, temperature and density sets and finally the vapour pressure at different temperatures are also read into the program.

The lap counter is set at zero and some of the temperature elements required for the matrix inversion are completed by statements 30 to 40. Initial values are set by statements 40 to 52 for CPSAT(6), its first increment, and very large values on SQBEST and SUMSQP for the proper execution of the first change in CPSAT(6). SQBEST and SUMSQP are related to the calculated sum of the squared errors.

The major part of the program in which the best value of CPSAT(6) is determined by trial and error is covered by statements 52 to 500. Matrix elements are calculated in statements 52 to 55. The values of the constants are calculated by matrix inversion.

The parameters and calculated pressures are stored in a separate array to determine the best set when the

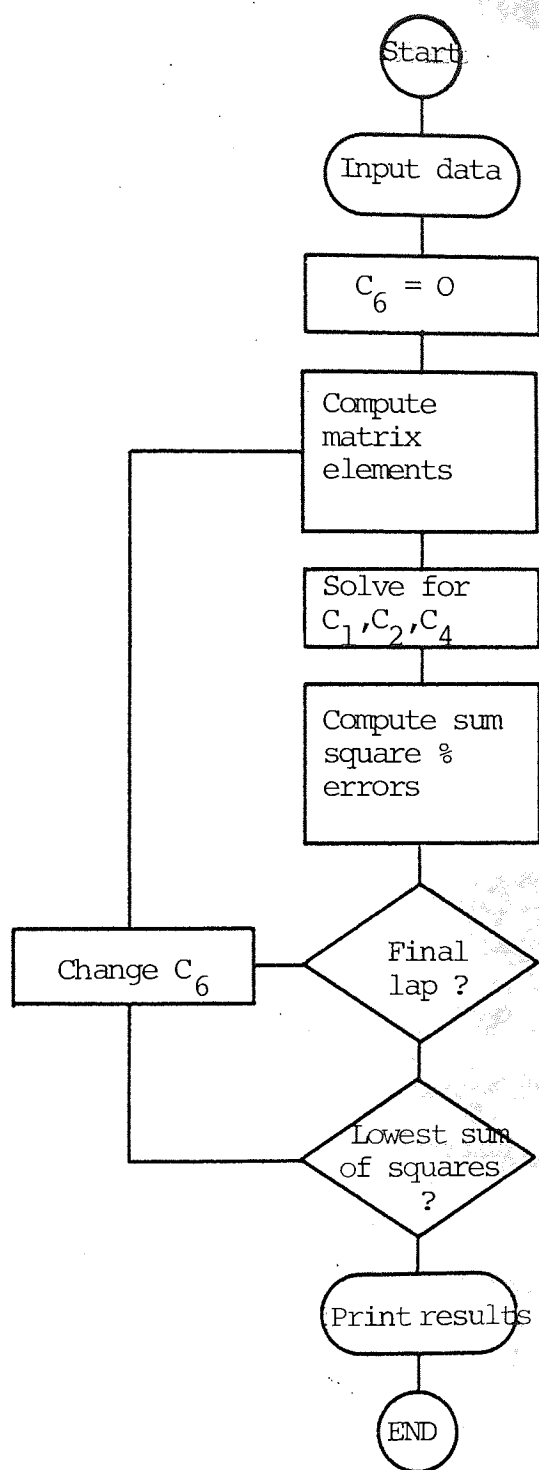


Figure 5.10 flow diagram of program VAPFIT

maximum lap number is passed or the best fit of the data is achieved. The value of CPSAT(6) is altered if the best set of data is not achieved and the matrix computation is restarted by transferring the program to statement 52.

Once the best value of the vapour pressure equation have been obtained, the final print out is entered at statement 500.

The flow diagram of this program is given in Figure 5.10 and a program listing in Appendix VII.

5.3.2 Binary Interaction Parameter Estimation

From the method described in Chapter 3, interaction parameters are required for the vapour-liquid equilibrium calculations. The analysis of the formaldehyde-water system and the formaldehyde-methanol-water system in terms of the constituent binary system taking into account the reaction products of the appropriate reactions have already been described in Chapter 3. The type of parameters for the different binary systems including the two condensable and noncondensable pair have also been described.

These parameters are required in different subroutines for the calculation of activity coefficients and fugacities for each of the species in the solution. The parameters are normally obtained by using an optimisation technique with the parameters as the unknown values.

The values of the parameters are initially guessed

and the vapour-liquid equilibrium calculations are performed and the calculated results are compared with the experimental results. The difference between the calculated and experimental results is used as a basis for the re-estimation of the parameters. When this difference is found to be less than the preset tolerance limit, the calculations are stopped and the current parameters are taken as the actual parameters.

An accurate set of experimental vapour-liquid equilibrium data is required for the parameter estimation. Several experimental data have been published for the formaldehyde system and considerable differences have been observed between the different reported data. The data reported by Olsson and Svensson (73) have been used for the formaldehyde-water system, because the data are thought to be more accurate due to the avoidance of superheating of the liquid. Also, the data can be presented in the form of a set of algebraic equations which can easily be used in the form of a computer program.

The equilibrium data reported by Walker (41) and Green and Vener (67) for the formaldehyde-methanol-water system have been used in this work. However, no accurate equilibrium data were observed for this system, where the ternary system is presented in the quinary format. However the mole fraction of all the significant components which exist in chemical equilibria in the two systems can be

calculated using the chemical reaction constants.

The composition of the ternary formaldehyde-methylene glycol-water system and the quinary formaldehyde-hemiformal-methanol-methylene glycol-water system resulting from the binary and ternary systems is calculated using the chemical reaction constants.

The same technique for the phase and chemical equilibria, as described in the section relating to the subroutine BUBLDILF is employed in the program for the parameter estimation. The difference in the parameter estimation program is that for convenience the subroutine BUBLDILF is divided into two smaller sections.

The program was first written for the parameter estimation of the ternary system and was later modified and extended for the quinary system. However, only the program for the quinary system will be explained because this program has been developed in a general form and can be applied to the ternary system by setting the mole fractions of hemiformal and methanol to zero in the data input field.

The calculations were first carried out for the ternary system because some of the binary parameters needed for the quinary system could be calculated independently in the ternary system. Thus the number of parameters which would have to be calculated in the quinary system calculations could be reduced. The Henry's constant for

formaldehyde-methylene glycol and formaldehyde-water, the single Wilson parameter for formaldehyde-water and the Wilson binary interaction parameters for methylene glycol-water have to be estimated.

Because the program for fitting the binary interaction parameters is based on the same theory used for the phase equilibria calculations, some of the subroutines which were used for the vapour-liquid equilibrium calculations are employed in this program. The subroutines are: RSTATE, ACTCO, PHIMIX, VIRIAL, INPUT and MODCON. These subroutines will not be explained again except for any necessary modifications required to make them compatible with the rest of the program.

5.3.3 Marquardt's Optimisation Procedure

Marquardt's optimisation technique is based on the minimum neighbourhood method in which an optimisation interpolation is performed between the Taylor series optimisation methods and the gradient search optimisation methods. The interpolation is used upon the minimum neighbourhood in which the truncated Taylor series gives an adequate representation of the nonlinear model. A set of nonlinear algebraic equations are obtained and these have to be solved for each iteration.

The theory upon which this method has been developed, has been explained by Marquardt (224-5). A modified version

of the computer program written by Kuester and Mize (225) has been used in this work.

Three segments, subroutines BMARQ, BSOLVE and function segment ARCOS, are contained in the program and these are described in the following section.

5.3.3.1 Subroutine BMARQ

Subroutine BMARQ is used for initialisation and control on the main optimisation calculations which are performed in subroutine BSOLVE. The information is communicated to or from this subroutine by the COMMON and CALL statements.

The subroutine is started with the transfer of information in the CALL statement namely the initial guess of parameters, the number of parameters, the number of data points, the value of the experimental pressures of the system and the sum of the squared errors. After the DIMENSION statements, the COMMON statements DECK and HAUL are used to communicate the information between this subroutine and the subroutine BSOLVE. The transfer variables are translated to the local variables in DO 42 and 43 loops. The minimum and maximum limits on the parameters are set in DO 12 loop. The calculation parameters are set equal to zero. The variable BV is set equal to one to indicate that the partial differentials of the function with respect to the parameters are calculated numerically in the subroutine BSOLVE. The variable ICON

is used as a flag to communicate the stage of optimisation from subroutine BSOLVE to subroutine BMARQ. The iteration number is contained in the variable ITER and is increased by one at every iteration. Subroutine BSOLVE is called at statement 200 for the calculation of the objective function and the estimation of new parameters. The WRITE statement is used for intermediate print outs. The value of ICON is checked by statements 10 to 50 to assess the condition of convergence.

Several messages can be printed out depending on the value of ICON. If the value of ICON is negative statements 10 to 40 are entered. If the value of ICON is minus one, no function improvement is possible. If the value is minus two, there are more unknowns than the functions. If the value is minus three, the total variables are found to be zero. If the value is minus four, the calculation has satisfied the convergence criteria, but the step length is still large. When the value of ICON is zero, the solution is reached. If the value is positive, the calculations are continued.

After the WRITE statements according to the value of ICON, the value of the parameters are stored in B1 matrix and the calculations are returned to the call statement for subroutine BSOLVE, for the next iteration.

The flow diagram of this subroutine is presented in Figure 5.11 and listing in Appendix VII.

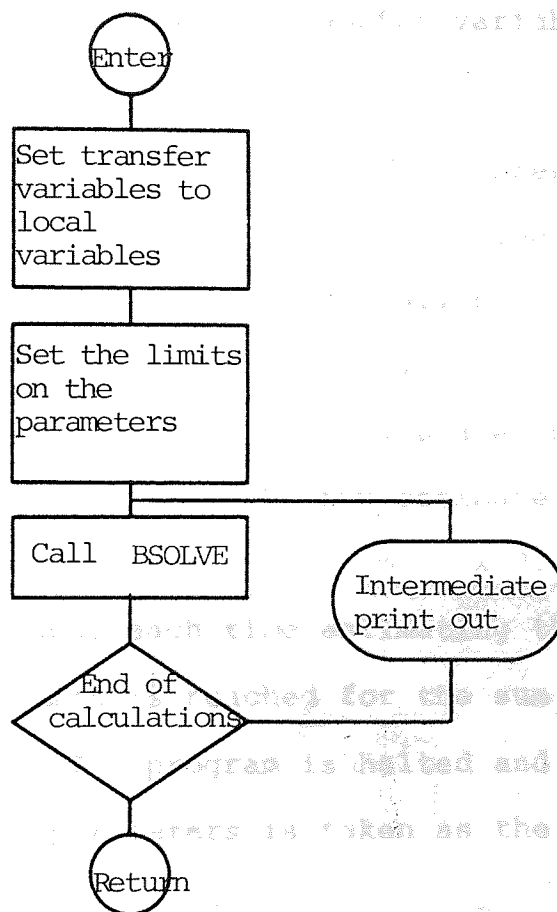


Figure 5.11 flow diagram of subroutine

BMARQ

5.3.3.2 Subroutine BSOLVE

After the DIMENSION and COMMON statements, the local variables are initialised and the transfer variables are transferred to the local variables.

For the first iteration the calculated pressure for each data set through subroutine EVALU is stored and the parameters incremented for the next iteration. In the second iteration the upper and lower limits are checked for the estimated parameters and the calculated pressure values are stored in matrix P. The new estimate for the parameters is calculated and stored in matrix P. The iterations are continued, each time estimating the parameters until the tolerance limit is reached for the sum of the square of the errors. The program is halted and the final estimate of the parameters is taken as the actual parameters.

A simplified flow diagram of the subroutine BSOLVE is given in Figure 5.12 and listing in Appendix VII.

5.3.4 Subroutin EVALU

This subroutine is used to coordinate the vapour-liquid equilibrium calculations with the parameter estimation section. Some of the preliminary calculations for the phase equilibria are also performed in this subroutine. Furthermore, the data from the main section and subroutine BSOLVE are translated to the variables used in the phase equilibria

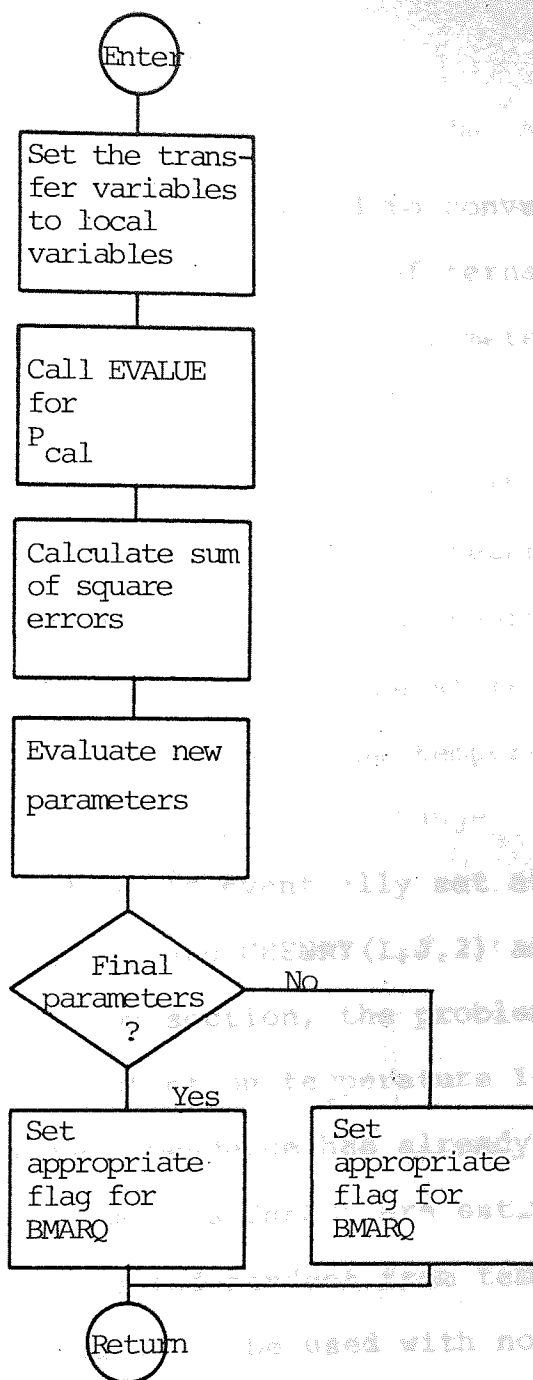


Figure 5.12 flow diagram of subroutine

BSOLVE

calculations.

A slight modification is required to convert this subroutine for the parameter estimation of ternary or quinary systems, since the names of the parameters are different in the two systems.

From the description of the subroutine INPUT and RSTATE, an interpolation and extrapolation technique is used in the program for the calculation of Henry's constant for each binary system at different temperatures. However, if Henry's constant is given at only one temperature, this value is used for the whole temperature range. In this case, the second Henry's constant is eventually set at zero. If the constants $\text{CHENRY}(I,J,1)$ and $\text{CHENRY}(I,J,2)$ are estimated in the parameter estimation section, the problem of the dependence of Henry's constant on temperature is solved because this temperature dependence has already been accounted for if the parameters CHENRY are estimated. These parameters are found to be independent from temperature and therefore isobaric data can be used with no further modification.

The values of PARAM are therefore set equal to CHENRY, rather than HENRY, defining the temperature dependence of Henry's constant.

The input and output information from subroutine BSOLVE, namely, the number of parameters NPARAM, parameter

matrix PARAM, number of data points NPTS, the calculated pressure XCAL2 and FV an extra location for transfer of desired variables are contained in the call statement for this subroutine.

The program is started with the DIMENSION and COMMON block statements SAIL 1, SAIL 2, SAIL 3, SAIL 4, SAIL 5 and FLEET. The value of input data and calculated pressure are contained in the COMMON block FLEET in this program in the form of matrices DATA and PCAL. The COMMON statements in this subroutine are used for communication purposes with the rest of the program except the parameter fitting section, BMARQ, BSOLVE and ARCOS.

The flag for subroutine PHIMIX is set at minus one at the start of the calculations. The parameters from subroutine BSOLVE are assigned to their proper form in the phase and chemical equilibria calculations.

The outer DO loop for the phase equilibria calculations is entered, covering the entire data points. The values of the experimental mole fractions of the vapour and liquid phases are stored in locations X and Y from the transfer variable DATA(J,1,K) and DATA(J,2,K), in DO 500 loop. The pressure and temperature of each data set are stored in locations P and T from the transfer variables DATA(J,3,1) and DATA(J,4,1). Subroutines VIRIAL and RSTATE are called using the already defined values of the liquid mole fractions and pressure with T as the given temperature.

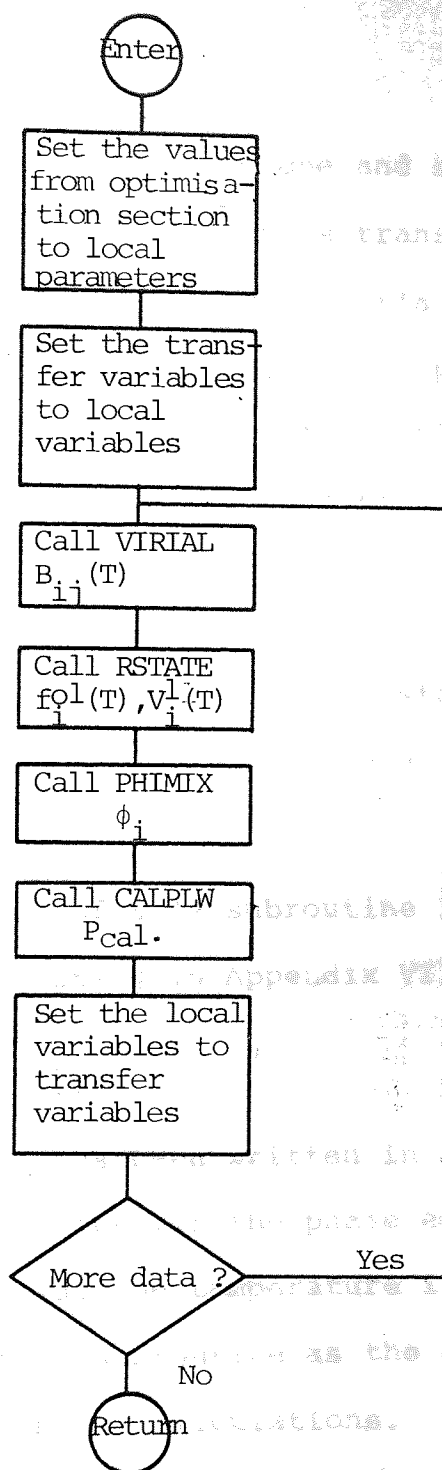


Figure 5.13 flow diagram of subroutine

EVALU

The value of SUMY is set equal to one and subroutine PHIMIX is called. The calculation is transferred to subroutine CALPLW for the phase equilibria calculations. The calculated values of pressure, vapour phase mole fraction, fugacity and activity coefficients are stored in the transfer variables in the appropriate COMMON block which is available in the main segment. The values of the calculated pressure are also stored in the transfer variable in the CALL statement which transfers these values to subroutine BSOLVE. The calculations are transferred by the RETURN statement to subroutine BSOLVE.

The flow diagram of this subroutine is given in Figure 5.13 and the listing in Appendix VII.

5.3.5 Subroutine CALPLW

This subroutine has been written in a similar manner to the subroutine BUBLDILF for the phase equilibria calculations except that the temperature iteration section is not included in this subroutine as the given experimental temperature is used in the calculations.

The subroutine is started with DIMENSION and COMMON statements SAIL 1, SAIL 2, SAIL 3, SAIL 4 and SAIL 5. The flag MARK for the subroutine PHIMIX is set at minus one and subroutine ACTCO is called. The fugacity of the vapour phase is calculated in DO 530 loop and the vapour phase composition is calculated in DO 550 loop. The calculated

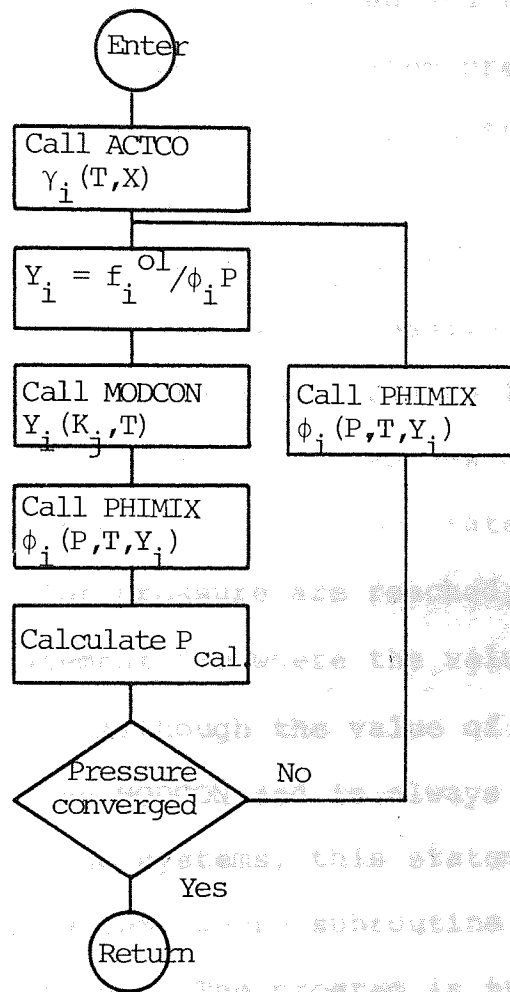


Figure 5.14 flow diagram of subroutine
CALPLW

vapour phase mole fractions are modified in subroutine MODCON according to the vapour phase chemical reaction equilibria. Subroutine PHIMIX is called and the value of pressure is stored in POLD. The system pressure is calculated with the current variables in DO 555 loop and its value is stored in P. The percentage error of the two successive pressure values is calculated and checked against a tolerance limit. If two successive calculated pressures are very close, within a tolerance limit the problem is solved. If the successive values differ, the iteration is continued starting from statement 520. When constant values for pressure are reached, the program is transferred to statement 570 where the value of SUMY is checked against unity. Although the value of SUMY is normalised in subroutine MODCON and is always made equal to unity for the reacting systems, this statement can be used for nonreacting systems where subroutine MODCON does not enter the calculations. The program is transferred to subroutine EVALU through the RETURN statement.

The flow diagram of this subroutine is given in Figure 5.14 and the listing in Appendix VII.

5.3.6 Main Segment For Calculation of Parameters, COMP5

This segment is mainly used for reading the experimental data and the final print out of the calculated results. The data are read into a common matrix DATA at a proper location.

The program is started with DIMENSION and COMMON statements SAIL 1, SAIL 2, SAIL 3, SAIL 4, SAIL 6 and FLEET. The subroutine INPUT is called to read the pure component data. Arbitrary values are set for the unknown values which are required in subroutine INPUT as these values are disregarded and only the parameters from the optimisation section of the program are used for the calculations. The number of data points, number of parameters and a flag for the indication of the units of pressure are read in the next statement. The title of the program is printed out for the initial heading of the computer output. A double DO loop 520 and 511 is entered for the data input. The data are read in the matrix DATA (I,J,K) where I indicates the number of data points, J is varied from one to four relating to liquid phase mole fraction, vapour phase mole fraction, pressure and temperature respectively. The variable K is set as the number of component. The values of pressure and temperature are stored in the first location of the section for the particular data set, DATA (I,3,1) and DATA (I,4,1) respectively. Subsequently the locations DATA (J,5,K), DATA (J,6,K) and DATA (J,7,K) are used to store the values of the calculated vapour phase mole fractions, vapour phase fugacity and activity coefficients.

The initial guess of the parameters are read in DO 518 loop. The value of the experimental pressures are

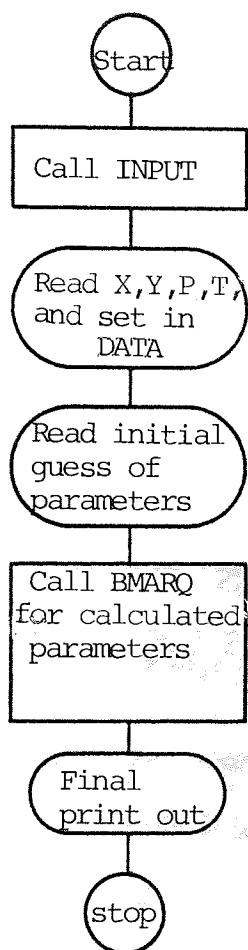


Figure 5.15 flow diagram of program

COMP5

stored in the transfer variable DUMP. The subroutine BMARQ is called for the remainder of the calculations. When the calculations have returned to this segment after the CALL statement for BMARQ, all the calculations are performed to evaluate the parameters. The section for the final print out is entered to communicate the experimental properties, the calculated variables and the obtained parameters. The calculations are halted after this section.

The flow diagram of this program is given in Figure 5.15 and a listing in Appendix VII.

5.4 MULTICOMPONENT DISTILLATION PROGRAMMING

The procedure and the theory of solution of a flow distillation column has been explained in Chapter 4. However, in this section the numerical solution of the equations obtained in Chapter 4 is discussed. The phase equilibria calculations which have been described in earlier sections, together with some subroutines for the solution of the distillation column are employed in the program.

The tray to tray method of solution is explained making reference to the discussion in Chapter 4. The Newton-Raphson method was used for the solution of each tray based on the model proposed in Chapter 4. In this program, some extra pure component physical properties

are needed such as the vapour and liquid phase enthalpies as a function of temperature and composition of the given phase. The explanation is given in the next section.

In this program, provision is made for including multiple feeds to any stage. Also any value of heat input or output can be included for each stage.

In the calculations the number of trays, reflux ratio, heat input to the boiler, flow rates of feed and bottom product and plate hold ups are taken as the given information. In turn the calculations are started in the program using the given information and the temperature profile, composition profile for vapour and liquid phases, flow rates profile and top product composition and flow rate.

The calculated values can be compared with the experimental values so that the accuracy and performance can be assessed for the calculation technique.

5.4.1 Subroutine NEWTON

The nonlinear set of simultaneous equations as developed in Chapter 4 are solved by this subroutine. The Newton-Raphson technique of solution is used for this purpose. The nonlinear set of equations are linearised and set in a matrix form and solved by the Gauss elimination technique. The solution is iterated until no change is

obtained in the calculated values.

The linearised matrices and the technique are described in Appendix IX.

The call statement is used at the beginning of the subroutine for the transfer of information. The maximum number of allowable iterations, M, is used to stop the calculation when no convergence has been achieved for the given number of iterations. The number of unknowns, N, is set to nine as there are nine unknowns and nine equations. The initial guess of variables XA, XB, XC, XD, XE, XF, XG, XH and XI is given to this subroutine in this statement. After convergence has been reached, these locations are used to contain the solution of the equations to be transferred to the main segment. The number of iterations, used for the solution of nonlinear equations, are contained in the variable ITER.

After the DIMENSION statements; several variables are contained in the COMMON block, TRAY 14, for the definition of the coefficient of matrices.

Following the COMMON statement, the transfer variables are stored in local variables. The matrix A which contains the coefficients of the linearised equations, is initialised by setting all its elements to zero. The partial differential values of the equations are stored in the elements of matrix A. The constants of the linearised

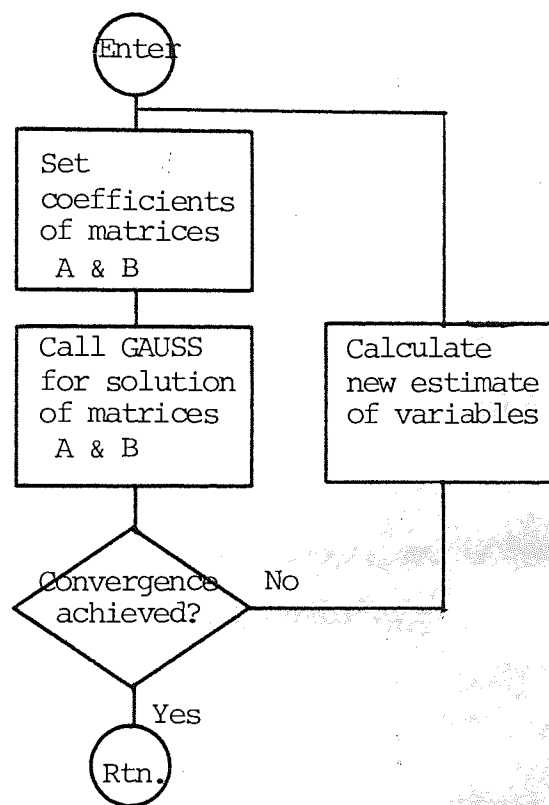


Figure 5.16 flow diagram of subroutine
NEWTON

equations are stored in matrix B. The subroutine GAUSS is called for the solution of matrix A. The solution is returned

Correction factors for the variables are obtained from the solution of matrix A. If the correction factors are less than the tolerance limit, convergence has been reached and the program is transferred to statement 60 where the calculated variables are stored in transfer variables and the program is returned to the main segment.

If the convergence is not achieved, the values of the variables are corrected and the solution is repeated starting from the DO 40 loop.

The flow diagram of this subroutine is given in Figure 5.16 and a listing in Appendix VIII.

5.4.2 Subroutine GAUSS

This subroutine is needed to solve linear simultaneous equations using the GAUSS elimination technique.

The transfer variables N, A, B and Y are contained in the CALL statement for this subroutine where N is the number of unknowns, A and B the matrices containing the coefficients of the partial derivatives matrix and variable Y is used to store the solution of equations.

After the DIMENSION statements, the calculation for the Gauss elimination is commenced using the matrices A and B. The calculations are terminated at statement 60.

The value of Y or the solution of matrix A is calculated in the following statement and the program is returned to the CALL statement for this subroutine through RETURN statement.

In this subroutine provision is made to stop the calculations when the linear equations are not independent. A WRITE statement is used to print a message when this situation is reached. This condition is encountered when a diagonal element of the A matrix is equal to zero after the elimination. The DO 60 loop is used for this purpose.

The listing of this subroutine is given in Appendix VIII.

5.4.3 Subroutine HTCNT

Subroutine HTCNT is used to calculate the molar enthalpies of both liquid and vapour phases for a given temperature and composition, starting from the heat capacity. The enthalpy factor is defined as a thermodynamic property. A thermodynamic property is defined as having the important distinction, that the difference between any two states is independent of the path chosen to pass from one state to another. This property is used for the calculation of the liquid phase enthalpy since the heat capacities of gases can be estimated more accurately than the liquid phase. The difference between

the enthalpies of the saturated vapour and liquid phases is defined to be the heat of vaporisation and this can be estimated easily for the hypothetical components methylene glycol and hemiformal.

It is assumed that the enthalpies are a function of composition and temperature only because the pressure is constant in the isobaric calculations. For simplification it is also assumed that the ideal liquids law can be applied to the system.

For non ideal systems, the heat of mixing of the liquid components must be used in the calculation of enthalpies. The heat of mixing is found to be small when compared with the heats of vaporisation and reaction. Therefore serious errors are not caused by neglecting the heat of mixing in the calculations.

The enthalpy of a pure component in the vapour phase is calculated from equation 5.16

$$\Delta H_i^V = \int C_{p_i} dT \quad (5.16)$$

where C_p is the heat capacity and is given as a function of temperature in the form of equation 5.17.

$$C_p = Ch1 + Ch2 T + Ch3 T^2 \quad (5.17)$$

where Ch1, Ch2 and Ch3 are the empirical constants for this equation. The values of the constants for each component and the method for their estimation are described in Appendix V.5. When equation 5.17 is substituted into equation 5.16 and integrated, equation 5.18 is obtained

$$\Delta H_i^V = Ch1(T-T_1) + Ch2 \frac{(T^2-T_1^2)}{2} + Ch3 \frac{(T^3-T_1^3)}{3} \quad (5.18)$$

where T_1 is the reference temperature.

The enthalpy of a mixture according to the assumptions, mentioned earlier, can be calculated from equation 5.19 for both vapour and liquid phases.

$$\Delta H_m = \sum_{i=1}^m \Delta H_i X_i \quad (5.19)$$

where ΔH_m is the enthalpy of the mixture, ΔH_i is the enthalpy of pure component i and X_i is the mole fraction of component i.

The enthalpy of the liquid phase can be calculated knowing the enthalpy of vaporisation. The value of the enthalpy of vaporisation and the method for their estimation are given in Appendix V.6. Equation 5.20 is used for the calculation of pure component i in the liquid phase.

$$\Delta H^L = \Delta H^V - DHV \quad (5.20)$$

where DHV is the enthalpy of vaporisation.

The program is started with the CALL statement, containing variables X, NCOMP, HT, T, FL and HTP. The mole fractions are contained in matrix X. The number of components are denoted by NCOMP. HT is used for the molar enthalpy of the mixture. The temperature is contained in T. FL is used as a logical flag for indicating the type of the phase. The molar enthalpy of the pure component is stored in HTP.

After the DIMENSION statements, the COMMON block TRAY 1, TRAY 11 and TRAY 13 are used to provide the subroutine with the necessary information.

The calculation of HTP values using equation 5.18 are carried out at the beginning of the program in DO 100 loop. The value of FL is checked and for the vapour phase the calculation is transferred to statement 90 and for the liquid phase equation 5.20 is used. The mixture enthalpy is calculated using equation 5.19.

The program is returned by the RETURN statement when the calculation for the enthalpy of the mixture is completed.

The flow diagram of the subroutine is given in Figure 5.17 and listing in Appendix VIII.

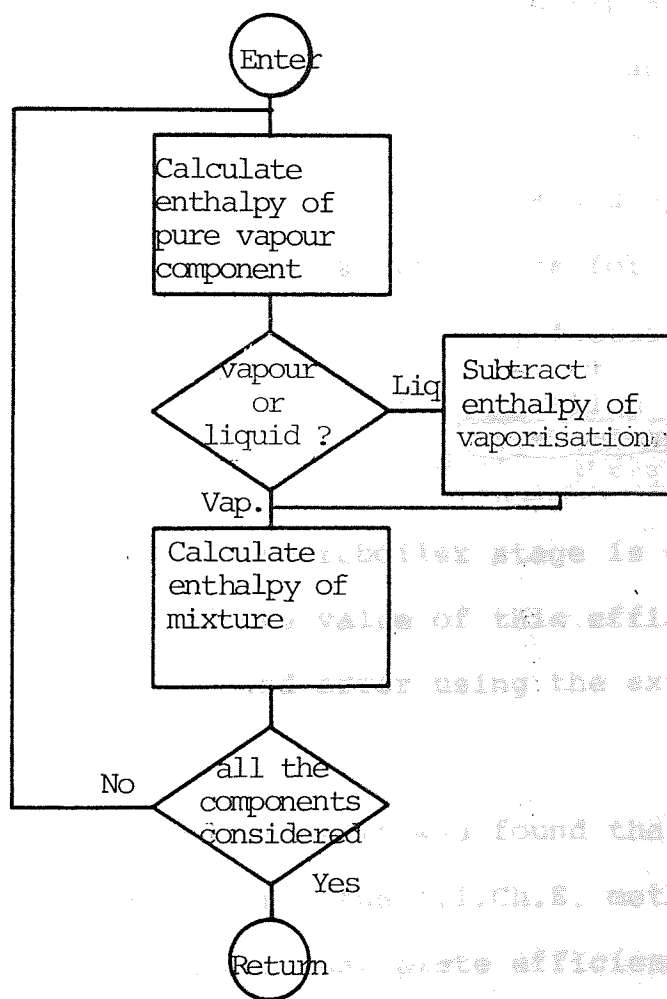


Figure 5.17 flow diagram of subroutine

HTCNT

5.4.4 Subroutine EFFICIENCY

The subroutine EFFICIENCY is required for the calculation of the efficiencies of the sieve plates in distillation column. The subroutine is based on the A.I.Ch.E. method and the theory has been explained in Chapter 4. The physical properties of the vapour and liquid phases are also calculated in this program and this has been explained in Chapter 4 and Appendix IV. Provision is made in this subroutine for the correction of the calculated efficiency factors depending on the specified variables, the feed location and the number of trays.

The efficiency of the reboiler stage is calculated using equation 4.82 and the value of this efficiency has been found by trial and error using the experimental data from this work.

During the calculations it was found that the plate efficiencies calculated from the A.I.Ch.E. method were higher or lower than the actual plate efficiencies depending on the position of feed plate. The procedure for the evaluation of the actual efficiency factors and the modification of A.I.Ch.E. efficiencies are discussed in Chapter 7.

The calculations were performed by adjusting the efficiency factor and proceeding with the column

calculations. The guessed plate efficiency was used in the calculations and the initial guess was improved by comparing the calculated and experimental results. The difference between the efficiencies calculated from the A.I.Ch.E. method and the actual efficiencies was found to be linear function of the feed plate position and the total number of plates.

The variables I and VMIX, where I is the stage number and VMIX the vapour molar volume at the stage temperature are contained in the CALL statement for this subroutine and are followed by the DIMENSION and COMMON statements TRAY8, TRAY9, TRAY10, TRAY15, TRAY16 and TRAY17.

The value of I is checked at the beginning of the calculations. If I is equal to one, the reboiler efficiency is calculated in the form of equation 4.82 and the program is transferred to statement 135 where the values of the vapour phase mole fractions are modified in the subroutine MODCON for the calculation of the composition at chemical equilibria. Because the equilibrium compositions of the vapour phase are modified by the efficiency values the calculations in MODCON are used for the evaluation of the equilibrium compositions.

The calculations for stage two to NTRAY-1 are carried out from statement 5 where UG or the vapour rate is calculated. The location YR is used for storing the

actual vapour phase mole fractions from the previous iteration. As the value of YR is not defined in the first iteration, it is set equal to YR2 or the mole fraction at equilibrium.

The average molecular weight is calculated in DO 10 loop. The vapour phase density RG is calculated and used in the calculation of the F factor, FFT. The DO 20 loop is used for the calculation of the liquid phase molar volume. The liquid rate per width of the tray, ELL, is calculated. The DO 30 loop is used for the calculation of the slope of the equilibrium curve and the ratio of the slope of the equilibrium curve to the slope of the operating line is calculated. The height of foam, clear liquid and liquid residence time, HF, HL and TL respectively, are calculated.

The viscosity of the pure liquid component and the viscosity of the liquid mixture are calculated from the relationships developed in Appendix IV.1. The double DO loop 50 and 40 are entered for the calculation of the liquid phase diffusivity using the equations given in Appendix IV.3, followed by the calculation of the liquid phase transfer unit TUNL.

The vapour phase viscosities are calculated in DO 60 loop. The viscosity of the vapour mixture is calculated in DO 80 loop. The DO 120 loop is entered and

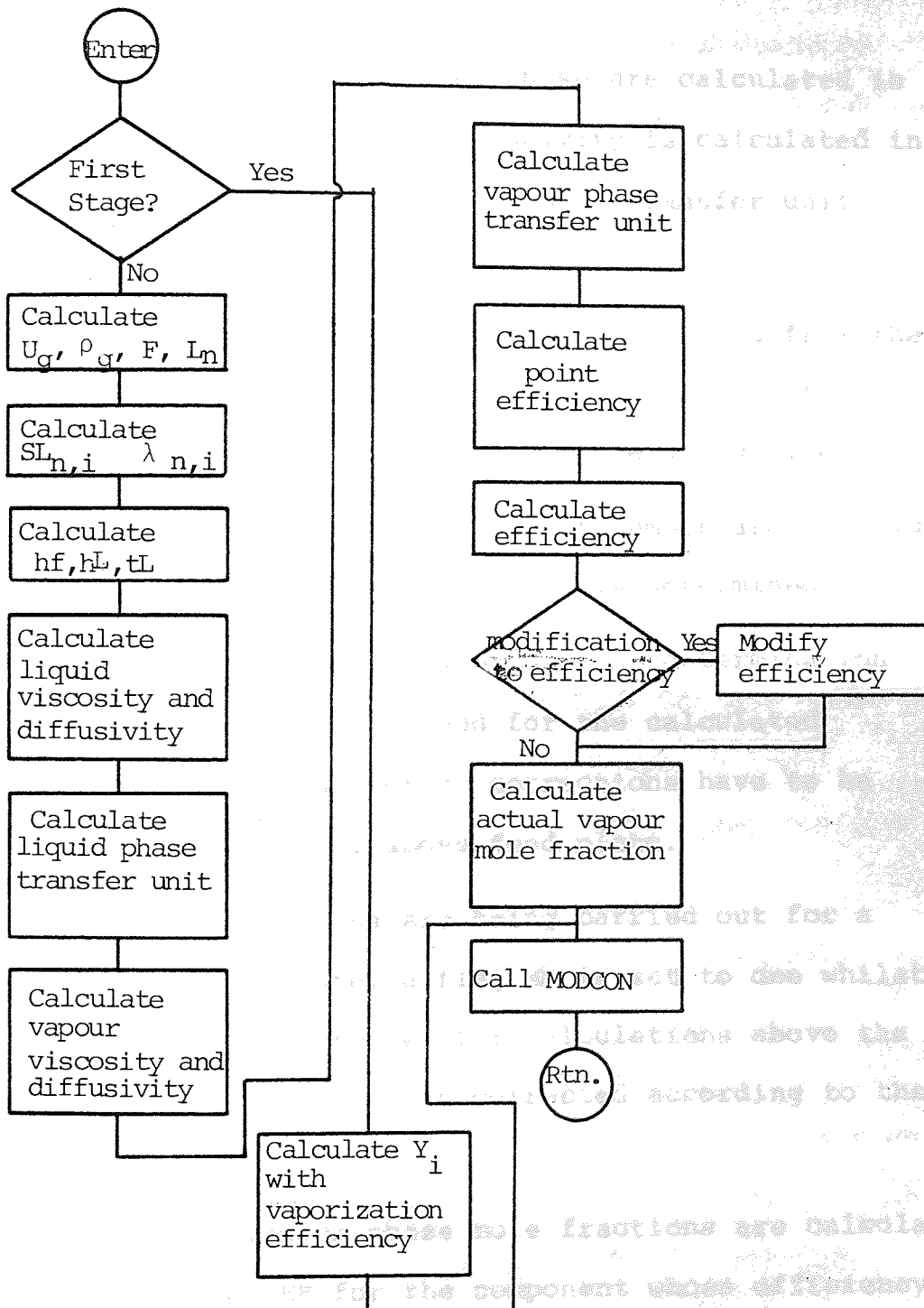


Figure 5.18 flow diagram of subroutine
EFFICIENCY

all the components in the vapour phase are calculated in this loop. The vapour phase diffusivity is calculated in DO 90 loop followed by the vapour phase transfer unit TUNV.

The point efficiency, PEFF, is calculated from the vapour and liquid transfer units and the ratio of the slope of the equilibrium curve to the operating line.

The eddy diffusivity and Peclet number are calculated and the efficiency of the plate, EFF, is determined.

Two IF statements are used for the determination of the type of correction needed for the calculated efficiency factors as different corrections have to be applied to trays below or above feed plate.

If the calculations are being carried out for a tray below the feed plate, a flag MN is set to one whilst the value of MN is set to two for calculations above the feed plate. The efficiency is corrected according to the value of MN.

The actual vapour phase mole fractions are calculated using the variable NEF for the component whose efficiency is evaluated by the difference of the mole fractions. The value of NEF is provided in the input data, read by subroutine INPUT.

The statement 135 is now entered where the actual

vapour phase mole fractions are modified by subroutine MODCON for the calculation of the actual vapour phase mole fractions which are at chemical equilibrium. The calculations are transferred by the RETURN statement to the subroutine BUBLDILF.

The flow diagram of this subroutine is given in Figure 5.18 and a listing in Appendix VIII.

5.4.5 Subroutines PRINT and WPRINT

These subroutines are required for the intermediate and final printout of the results. Entry to subroutine PRINT is controlled in the main segment. Certain flags are set in the main segment, where this subroutine can be used for printing intermediate results at any desired iteration step.

The subroutine PRINT is started with the DIMENSION and COMMON statements TRAY7, TRAY8, TRAY9, TRAY10 and TRAY17. Firstly, a full page is given and the headings printed at the top of the page. Then the components under distillation, the iteration number, the stage number, the number of internal iterations are printed out and the final print out is indicated by built in WRITE statements.

The results for each stage with the appropriate headings are printed, including the reboiler, feed plate and the condenser. At the end of calculations, after the print out, the subroutine WPRINT is called and the compositions of

all the components are converted in weight percents to the original binary of formaldehyde-water and the original ternary of formaldehyde-methanol-water. These values are printed for the vapour and liquid phases leaving each stage together with the stage temperature.

The printouts from subroutine WPRINT can be compared directly with the experimental results, with no need for any further conversions.

The listing of the programs PRINT and WPRINT are given in Appendix VIII.

5.4.6 Main Segment For Distillation Calculations, CHEMICOL

This segment is used for reading the specified variables for a particular case, creating the profiles for the initially guessed values, setting the flags, and performing all the calculations by referring to various subroutines.

The program is started with the DIMENSION and COMMON statements TRAY1, TRAY7, TRAY8, TRAY9, TRAY10, TRAY14 and FLEET for the transfer of variables. The type of variables, the logical variables and the function statements are defined. The function statements are used to define the liquid phase chemical reaction constants as a function of temperature.

The logical flags FLF, FLL and FLV are defined as FALSE, FALSE and TRUE, to be used in subroutine HTCNT

where these variables refer to the feed, liquid and vapour streams respectively. The liquid phase is indicated by the FALSE values and the vapour phase by the TRUE values.

The values of IFLG and IFIN are set to zero, these being the flags for subroutine INPUT and subroutine PRINT. The experiment's code, the title of the program and printing interval are read in, setting NPRINT at zero, which is the variable to be incremented by one at each printing interval. The number of components, NCOMP, number of stages, NTRAY, the number of feed tray, ITRAY and the number of light components are read in. The iteration number for condenser ITER(NTRAY) is set at one because the equation for this stage is linear and no iterative solution is required. The maximum number of iterations in the Newton-Raphson solution M, and the number of equations N, the reference temperature TREF, and the pressure PN are read in. The DO 700 loop is used to read the amount of heat transferred to each stage. The values of Q(I) are all set at zero except the reboiler and condenser stages. The molar heats of reaction DRL1 and DRL2 are read in. The feedflow rate temperature and composition are set equal to zero for all the trays in DO 710 and 711 loops. The coefficients for equation 5.18 are read for all the components. The feed flow rate FFD, temperature TF and composition XRF are read for the location of the feed tray ITRAY. The bottom product flow rate, temperature and composition are read for location one in

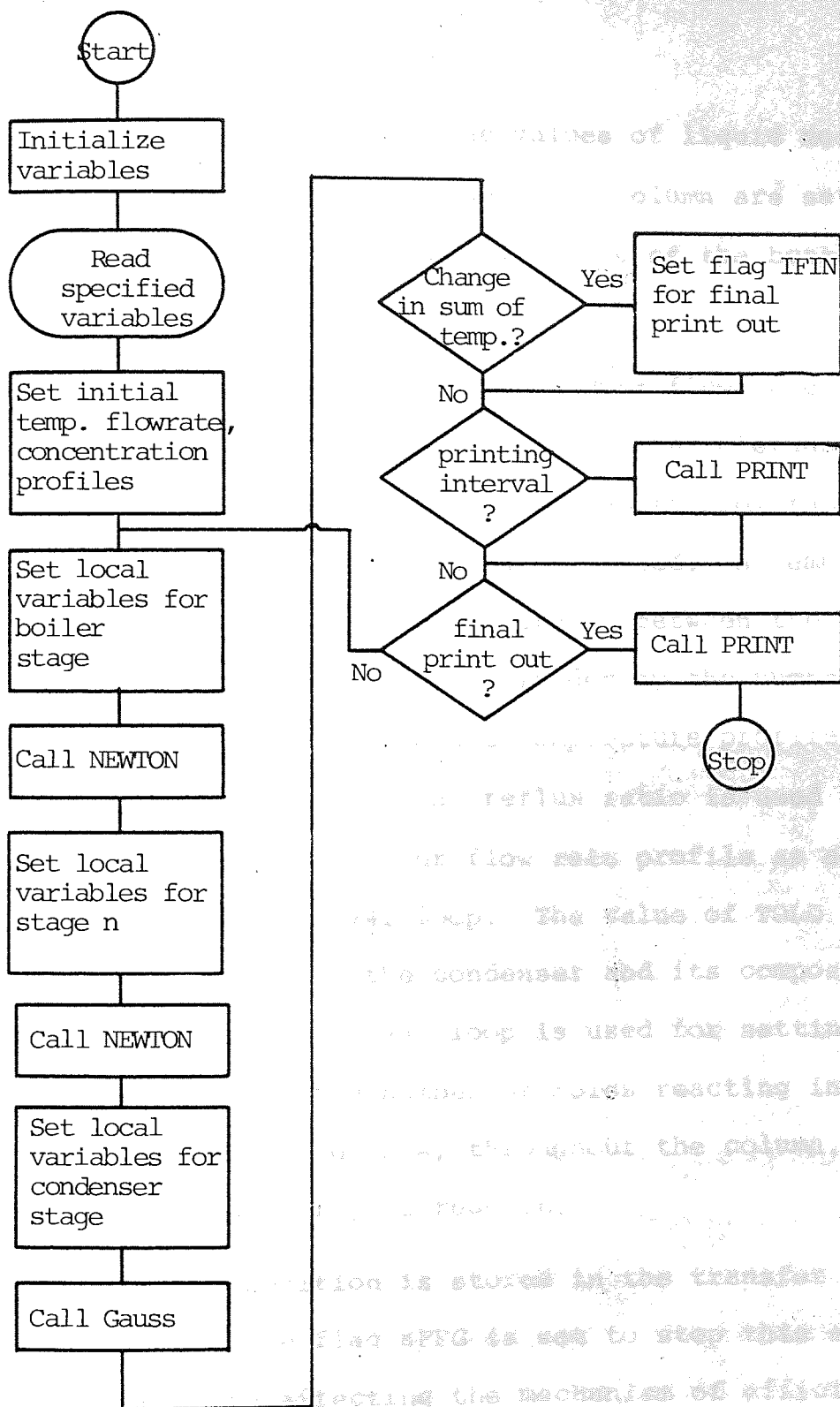


Figure 5.19 flow diagram of program

CHEMICOL

their appropriate matrices. The values of liquid mole fractions and flow rate throughout the column are set equal to the mole fraction and flow rate of the bottom product in DO 740 loop.

The reflux ratio RRATIO, top product flow rate PRT and its temperature TPRT are read. The tolerance limit on the column calculations ERR and the tolerance limit on the stage calculations E2 are read. A temperature difference is defined as the difference between the top and bottom product temperatures divided by the number of stages in order to calculate the temperature profile for the initial estimate. The reflux ratio is used for the calculation of the vapour flow rate profile as an initial estimate in DO 741 loop. The value of TOLD and vapour flow rate out of the condenser and its composition are set at zero. The DO 745 loop is used for setting an initial estimate for the number of moles reacting in the two reactions, ALFA and BETA, throughout the column. The weir height on each tray is read in.

The feed composition is stored in the transfer variable XI2 and the flag EFFG is set to stop this stage of the calculation affecting the mechanism of efficiency calculations. The subroutine BUBLDILF is called for the calculation of the enthalpies of vaporisation for the feed stream. The subroutine HTCNT is called to calculate

the enthalpy of the feed. The counter for the total number of iterations IS is set at one for the first iteration. The column calculations are started from statement 20.

The composition of the liquid phase for stage one is stored in transfer variable XI2 and subroutine BUBLDILF is called for the calculation of the vapour phase leaving stage one and its temperature. The subroutine HTCNT is called for the liquid phase leaving stage one, the vapour phase leaving stage one and pure component enthalpy for the liquid entering stage one at temperature T(2).

The chemical reaction constants at temperature T(2) are calculated and the current variables are set in transfer variables, Z, ZF, ZX, ZI and CNR for the calculation of the nonlinear equations in subroutine NEWTON. This subroutine is called and the calculated variables from the set of nonlinear equations are returned.

The DO 70 loop is used to repeat the same calculations for stages one to the top tray. The stage calculations are terminated at statement 70 where the condenser stage calculations start. Since no efficiency is calculated in the condenser stage the flag EFFG is set at FALSE. The subroutines BUBLDILF and HTCNT are called for the calculations of the condensed liquid. The coefficients of the linear equation for the solution of the condenser stage are set in matrices AMT and BMT where the subroutine

GAUSS is called for the solution of ALFA(NTRAY), BETA(NTRAY) and the flow rate of the condensate. The flow rate of the product is then calculated.

The convergence check is based on the difference between the sum of the temperatures throughout the column for two successive iterations. The sum of stage temperatures is calculated by DO 90 loop and its value is stored in TNEW. This value is compared with TOLD and the difference S is calculated. The value of TOLD is updated by TNEW. If the value of S is less than ERR, the tolerance limit, the flag IFIN is set at unity for the final printout. If convergence is not achieved, the variable NPRINT is incremented and its value is checked against IPRINT, the printing interval. If the NPRINT is equal to IPRINT, subroutine PRINT is called and NPRINT is initialised at zero. If these values are not equal but convergence has been achieved, the subroutine PRINT is called for the final printout. The value of IFIN is checked. If this value is equal to one, convergence has been achieved and the final printout has been performed and the program is halted. If convergence has not been achieved, the program is transferred to statement 20 where the calculations for the column are restarted using the variables calculated in this iteration as initial guesses.

The flow diagram of this segment is presented in

Figure 5.19 and a listing in Appendix VIII.

5.5 MODIFICATION OF PROGRAMS

Greater flexibility in the construction of the different programs is obtained by dividing the computer programs into specialised subroutines. The main programs for the calculations are obtained by the correct combination of these subroutines, as explained in previous sections.

The subroutines are used in three types of programs. Although the general form of the subroutines do not alter from one main program to another, some modifications are needed in order to apply the subroutines to the different programs. The modifications are required to alter the communication mode or any extra necessary calculations.

5.5.1 Modification of Programs for Parameter Estimation

The common subroutines between the phase equilibria and parameter estimation programs are VIRIAL, PHIMIX, RSTATE, ACTCO and MODCON.

Minor adjustments are needed to apply these subroutines to the parameter estimation programs. The COMMON statements need to be modified in these subroutines.

The COMMON block SAIL 5 is added to all the subroutines except ACTCO and MODCON.

Subroutine ACTCO is modified by including the COMMON statement SAIL 6. The COMMON block FLEET is excluded from subroutine INPUT. New variables DATA and PCAL are stored in COMMON block FLEET which transfer the variables between the main segment and subroutine EVALU.

Subroutine MODCON is unaltered.

5.5.2 Modification of Programs for Distillation Calculations

Subroutine BUBLDILF should be altered in order to calculate the phase equilibria in the distillation calculations. Two versions of this subroutine are used for the mathematical modelling of the system. BUBLDILF A is used for the calculation of the phase equilibria and BUBLDILF B is used for the calculation of the phase equilibria in the distillation column. Subroutine BUBLDILF A has been explained in Section 5.2.7. These modifications are as follows:

Extra variables EFFG and IT are included in the calling sequence of BUBLDILF B where EFFG is the flag for the efficiency calculations and IT is the stage number.

The name of COMMON blocks SAIL 1, SAIL 2, SAIL 3 and SAIL 4 is changed to TRAY 2, TRAY 3, TRAY 4 and TRAY 5 respectively. The contents of these COMMON blocks are unaltered.

Extra COMMON blocks, TRAY 1, TRAY 13, TRAY 16 and

TRAY 17 are added to allocate the variables in a common storage area. The COMMON block FLEET is unaltered, containing the flag for subroutine INPUT.

The intermediate and final WRITE statements for the phase equilibria calculations are excluded in BUBLDILF B. Subroutine OUTPUT is not included in the distillation column calculation and therefore the CALL statement for this subroutine is omitted.

After statement 710 in BUBLDILF A, extra segments are introduced for the calculation of the plate efficiency. The local variables are stored in transfer variables and the appropriate flags are checked for the calculation. The subroutine EFFICIENCY is called for the calculation of the efficiency of plate IT.

The enthalpy of vaporisation at the saturation pressure is calculated for each component using the relationships given in Appendix V.6. These values are stored in DHV(I) which in turn is located in COMMON block TRAY 13, to be used in subroutine HTCNT. The subroutine is terminated with the RETURN statement.

The listing of subroutine BUBLDILF B is given in Appendix VIII.

Subroutines RSTATE, PHIMIX, ACTCO and VIRIAL are also modified with the change of the name of the COMMON blocks SAIL 1, SAIL 2, SAIL 3 and SAIL 4 into TRAY 2, TRAY 3,

TRAY 4 and TRAY 5.

The subroutine MODCON is not altered and can be used without any modifications.

Subroutine INPUT should be modified to INPUT B, in order to be used in the distillation calculations. The name of the COMMON block is changed similar to the other subroutines. The extra COMMON block TRAY 15 is used to store the pure component data to be used in subroutine EFFICIENCY. A DIMENSION statement is also included for the definition of the size of matrices used in this COMMON block.

The program is not altered until statement 260, where the new read statements are introduced for the data needed in subroutine EFFICIENCY. The molecular weight, molar volume of pure liquid at normal boiling point, normal boiling temperature, the number of component whose efficiency is calculated by the difference, the factors for correction of calculated efficiency and the vaporisation efficiency for the boiler stage are among the extra pure component data.

The listing of subroutine INPUT B is given in Appendix VIII.

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PARATUS

6. EXPERIMENTS AND APPARATUS

6.1 INTRODUCTION

In the previous chapters, the formulation of a mathematical model for the distillation of formaldehyde-methanol-water solutions and the method for the solution of the model have been discussed in detail. The solution of the equations in the mathematical model was achieved by means of computer programs. The results from the solution of the computer programs were in the form of a series of temperature, concentration and flow rate profiles over the plates of the distillation column.

The performance of the developed programs could only be evaluated by comparing the calculations with some experimental results. Therefore a set of experimental results is required for this purpose.

Some limited sources of experimental data have been listed in Chapter 2. A resume of the reported data on the distillation of formaldehyde has shown that these data are very specialised and are not common to the data of an ordinary distillation column. Thus an existing distillation column with some alterations has been utilised to obtain sets of experimental results. The performance of the mathematical model can be evaluated by varying several parameters and comparing the experimental and calculated results.

The formaldehyde-methanol-water system was used for

the experiments since a more general approach is made possible using this system rather than the formaldehyde-water system. Furthermore, the distillation of a ternary system is encountered frequently in the commercial production of formaldehyde. However, the mathematical model can be applied to the binary system as well as to the ternary systems, by setting the concentration of hemiformal and methanol equal to zero.

The design characteristics of a distillation column which had been used for the investigation of simultaneous distillation and chemical reaction have been explained by Davies (89). However, that particular column has been considerably modified in order to overcome the existing difficulties in assembling and operating the column (89) and to increase the number of adjustable parameters. Thus a 1.5 m high, 0.076 m diameter, eight sieve plate glass distillation column was built.

6.2 DISTILLATION EQUIPMENT

The distillation unit is comprised of the column, reboiler, condenser, reflux divider, feed system, feed heater, condenser, control panel and the fume extraction unit. The feed was stored in a 0.1 m³ aspirator where the liquid flowed under gravity through the feed regulator valve, feed rotameter and feed heater to the required feed plate. The liquid overflow from each plate was directed to the externally adjustable weir and downcomer through

a side arm on the column.

Heat was applied to the reboiler by two 2kW stainless steel electric immersion heaters. The reboiler was formed from a 0.006 m^3 glass container. The bottom product was removed through an adjustable weir, a regulator valve and steam trap. The bottom product flow rate was determined by weighing and measuring the volume of the collected product over a given time at steady state conditions.

The liquid and vapour samples were taken from the sampling valve and analysed on the gas chromatograph. A cyclic multipoint temperature recorder was used to record the temperature of each plate and other important streams. The vapour leaving the column was condensed in 0.05 m I.D., water cooled condenser. The reflux was divided by an electrically controlled solenoid operated ball and socket valve. The frequency of the electronic impulses to the solenoid could be varied by a controller unit. The reflux was returned to the top plate whilst the weight and volume of the top product was measured over a given time period.

All the units except the feed reservoir, flowrators and control panel, were contained in a heated cabinet in order to minimise the heat loss. Thus the distillation process could be observed visually, as a hot air jacket was used as an insulator. The top of the cabinet was

connected to a fume extracting duct in order to minimise the release of formaldehyde fumes.

6.2.1 The Distillation Column

A glass distillation column consisting of two sections, each containing four glass sieve plates was constructed. Each section was 0.76 m long and had a diameter of 76 mm.

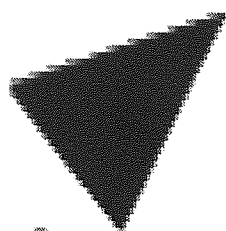
The eight sieve plates in the column were expected to give a reasonable separation of the components and the 76 mm diameter of the column was large enough to minimise the effect of drawing samples from the plate. Details of the column and each individual section can be found in figures 6.1 - 3.

The sieve plates were made from 2 mm glass, containing 208, 1.5 mm diameter holes with a radial pitch of 4.5 mm and a circular pitch of 4.35 mm, giving a free area of 8.1 per cent (see figure 6.4).

A plate separation of 152 mm was used in both the top and bottom sections whilst a plate separation of 208 mm was used between plates number four and five where a flange was required to connect the two column sections.

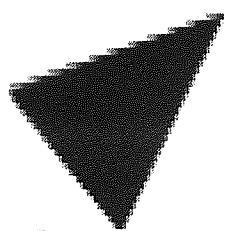
Access to each plate for the inlet, outlet, sampling and venting the downcomers was achieved by two S.V.L. 22 and S.V.L. 15 screw joints (174). The necessary connections were formed by the side arms with rigid and sliding joints (see figures 6.2 - 3).

The outlet of the plate to the weir and downcomer



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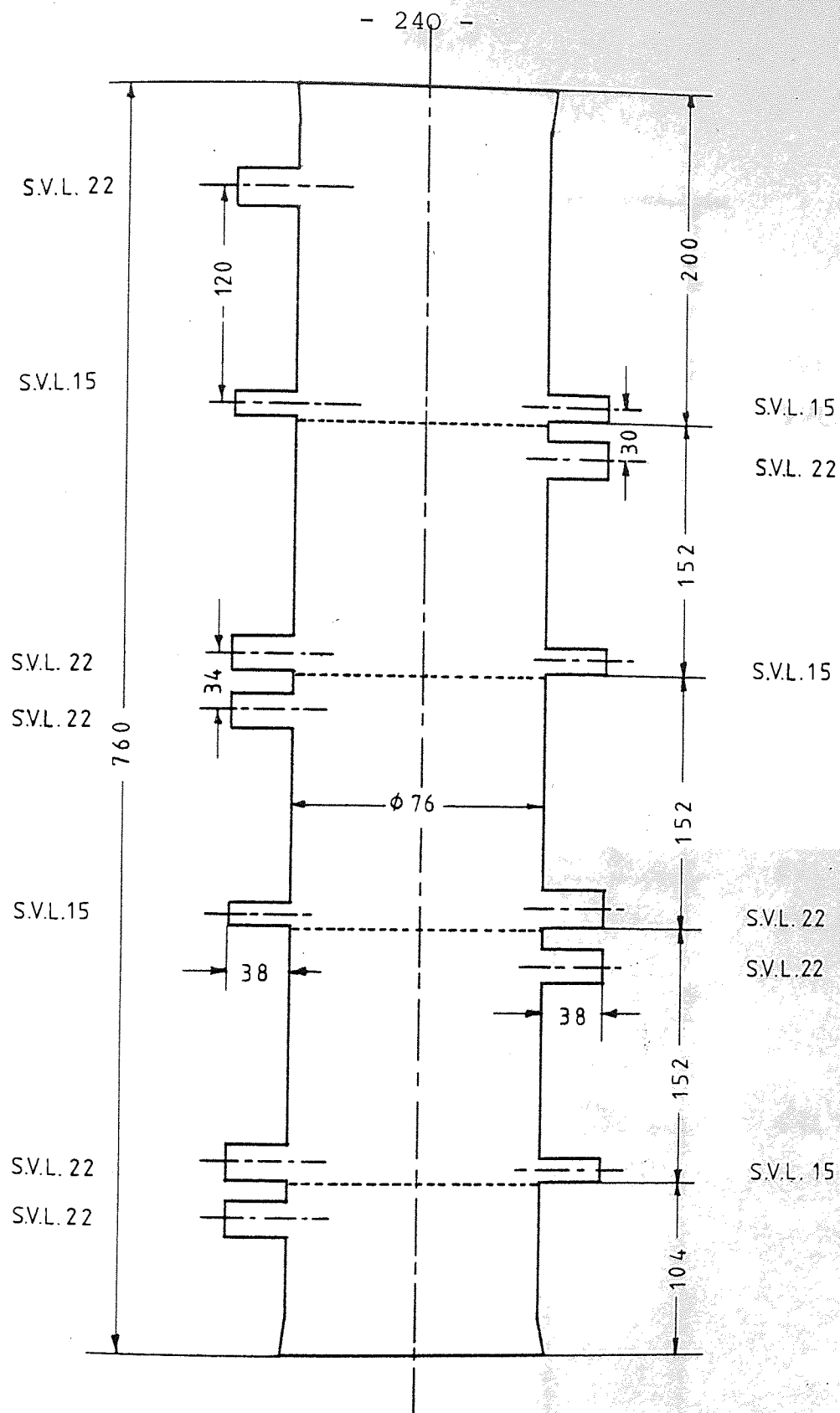


Figure 6.2 top section of column

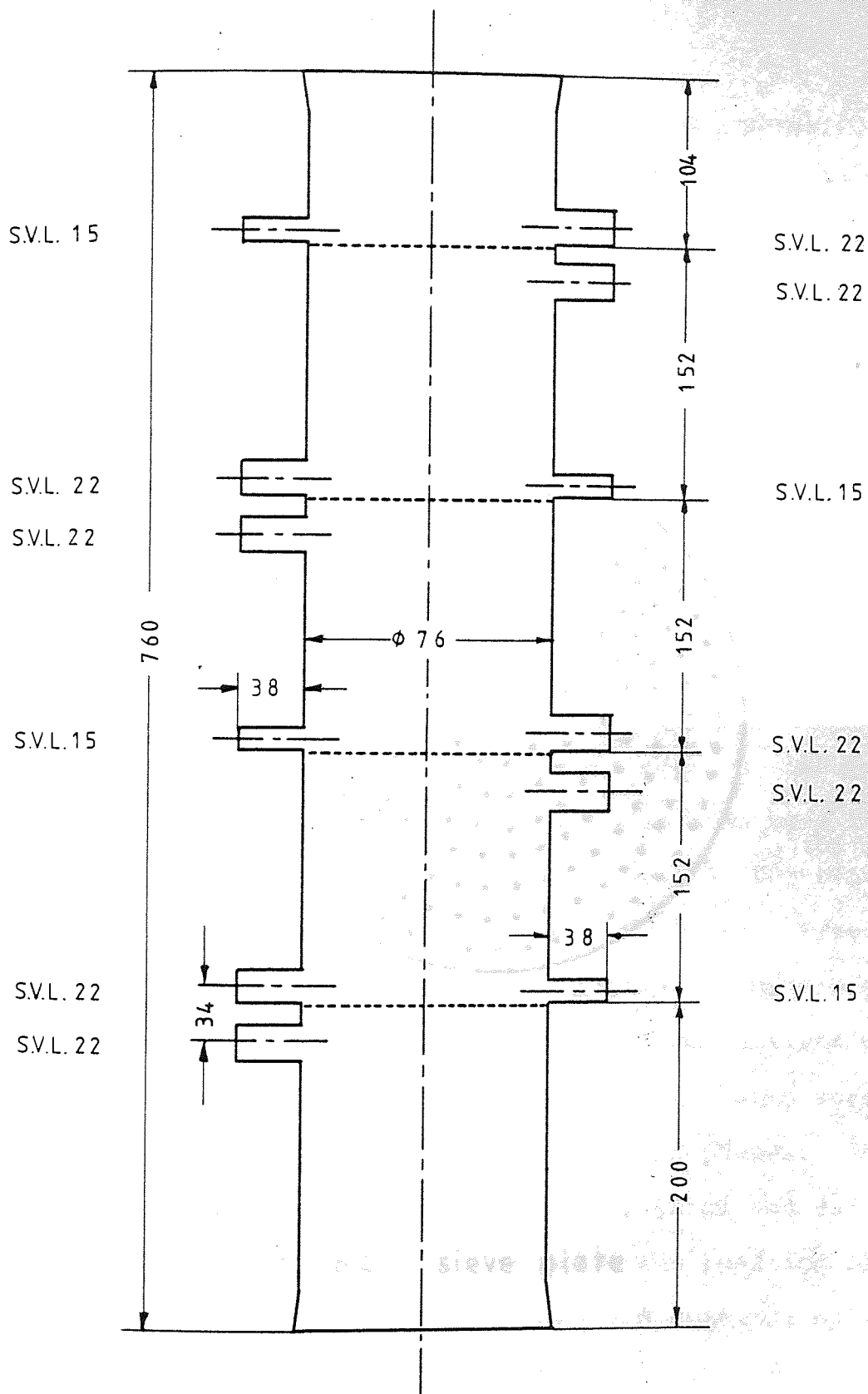


Figure 6.3 bottom section of the column

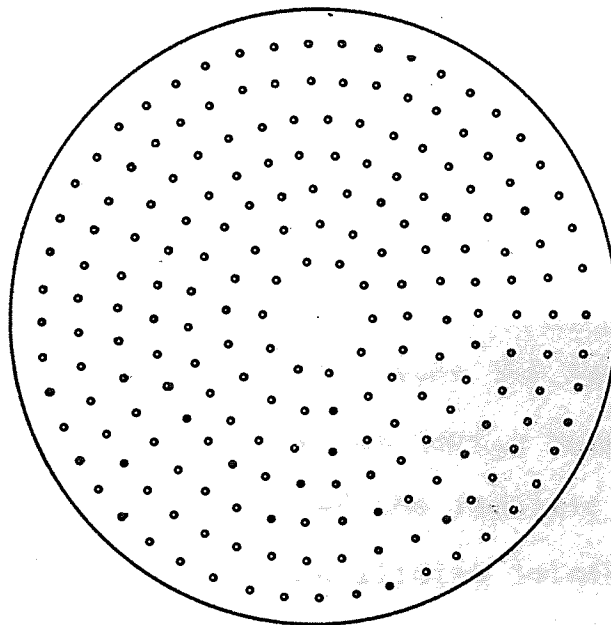


Figure 6.4 sieve plate

system was also used as the liquid sampling point. The vapour samples were withdrawn through the S.V.L. 22 sliding joints which served as the vent for the downcomers to break the syphoning effect.

6.2.2 The Side Arms Connections

The S.V.L. 22 and S.V.L. 15 opening in the column walls for each plate were connected to three different shapes of glassware made of S.V.L. 15 joints. These joints were used as the inlet to the plate from the downcomer of the plate above, the outlet of the plate, the adjustable weir system, access for the liquid and vapour sampling, the thermocouple pockets and the vent for the downcomers. The S.V.L. 15 and S.V.L. 22 screw joints were used because this type of glassware provided the facility for connecting two glass tubes with rigid and sliding joints. Freedom of movement in three dimensions was provided by the sliding joints for the glass tubing. Also better connections were provided for the glass side arms ^{and} therefore leaks were minimised from both the vapour and liquid phases. The most important advantage gained by the screw and sliding joints was the capability of changing the position of the sliding parts, according to the desired setting, without having to build a new set of connection tubes for different plate holdups. The new position was achieved by moving the inner tube along the sliding joints.

Three types of connections can be achieved using the S.V.L. screw joints, namely rigid butt connections, sliding connections and sealing connections.

The middle section of the side arm connectors was made in the shape of a cross from S.V.L. 15 screw joints. This section was connected to the outlet of the sieve plate which was also an S.V.L. 15 screw joint, by a rigid flange connection having a sealing ring in the middle. The upper arm of this section was connected to a 8 mm O.D. glass tube through a sliding joint with a bored cap and sealing ring of 8 mm I.D. The lower arm was connected to a 8 mm O.D. glass tube through a sliding joint forming the adjustable weir height. The inner 8 mm diameter glass tube could be moved up or down to give the desired weir height. The outer arm was connected to a 8 mm O.D. glass tube through a sliding joint, leading out of cabinet to a glass valve. The liquid was sampled through this connection (see figure 6.5).

The upper section of the side arm connector is made in a T shape from S.V.L. 15 screw joints. The plain side of this section was connected to the S.V.L. 22 vent opening on the column wall through a sliding joint. The lower arm of this section was connected to the 8 mm O.D. glass tube from the upper arm of the middle section through a sliding joint, forming the necessary connection for breaking the syphoning effect in the downcomer. The outer arm of this section was also connected through a sliding joint to a

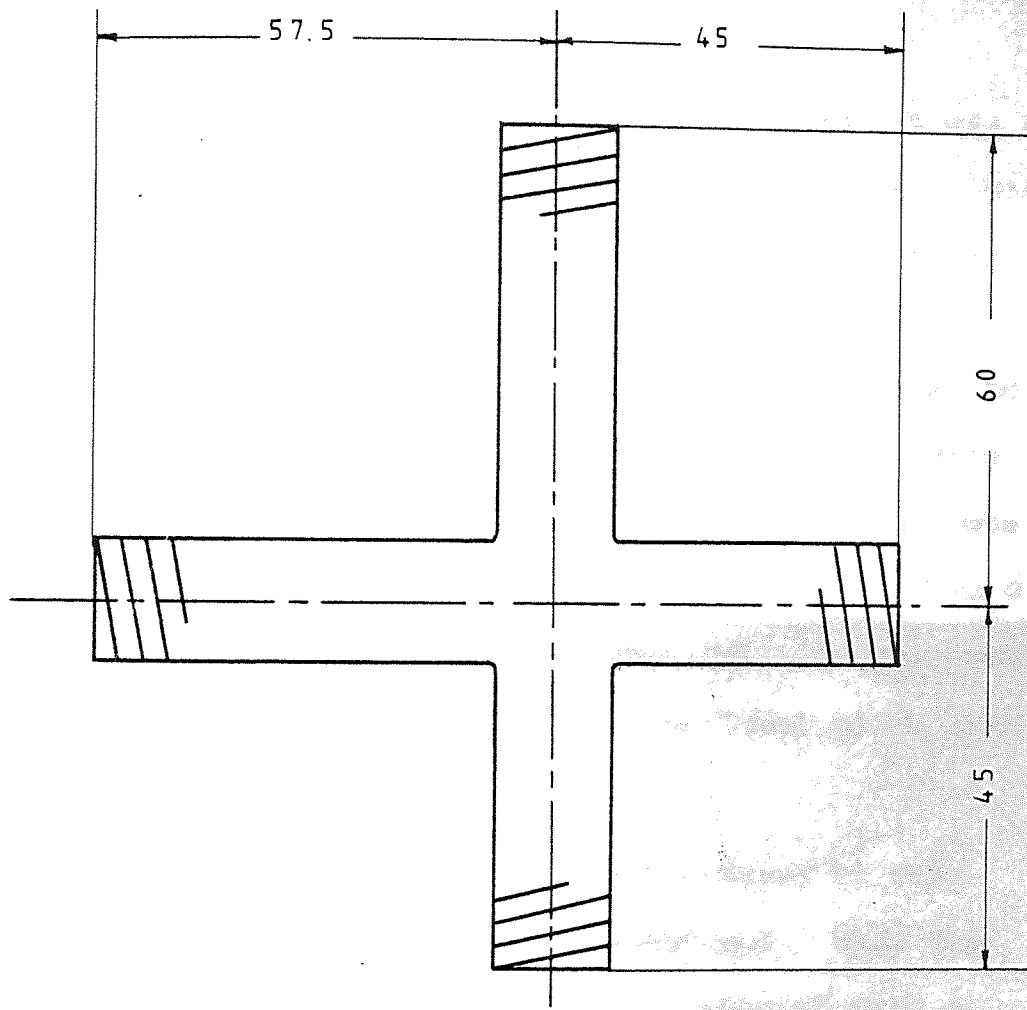


Figure 6.5 middle section of side
arm connector

8 mm O.D. glass tube leading out of the cabinet into a three way valve, forming the vapour sampling system (see Figure 6.6).

The lower section of the side arm connectors was also made of S.V.L. 15 screw joints in a T shape. The plain side of the section was connected to the inlet of the lower plate, which was made of S.V.L. 22, through a sliding joint. The upper arm was connected through a sliding joint to the 8 mm O.D. glass tube from the lower arm of the middle section, forming the downcomer of the plate. The outer arm was connected through a sliding joint to an 8 mm O.D. sealed glass tube forming the pocket for the thermocouple which measured the temperature of the lower plate (see Figure 6.7).

The necessary flexibility was provided by this configuration of the side arm connections. When the middle section of the side arm was connected with a rigid flange, the upper and lower sections could be positioned so that the 8 mm. O.D. glass tubes could be connected to the two sections without imposing any stress in either section. Flexibility in the side way direction was achieved by tilting the 8 mm. O.D. glass tube slightly, in the slide joints embedded in the sealing rings. Thus stresses in the finished column were reduced by the design of the external downcomer system. Sampling of the vapour and liquid phases could be achieved from outside the cabinet without interfering with any parts inside the

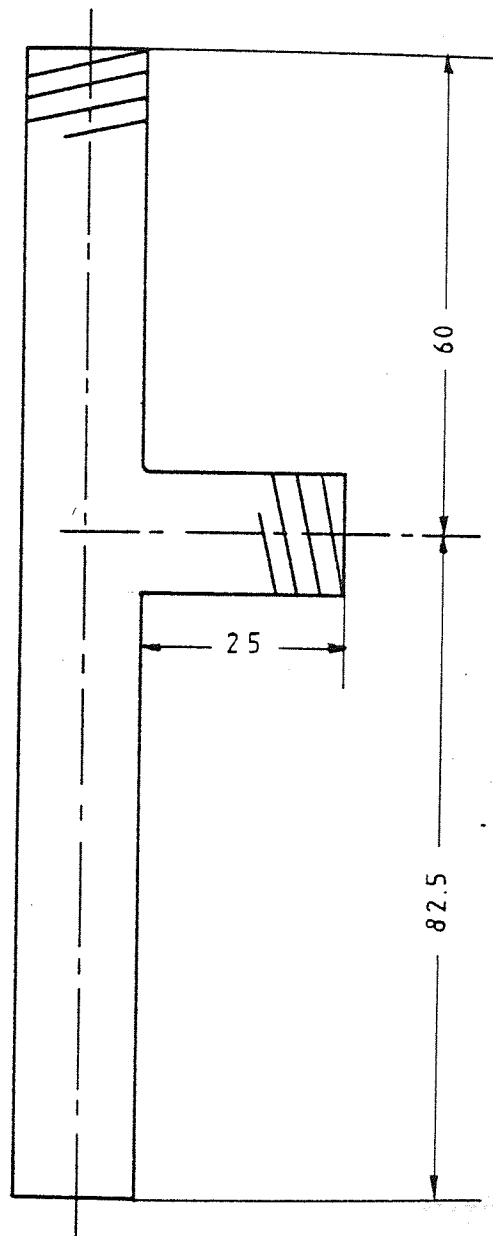


Figure 6.6 : top section of side
arm connector

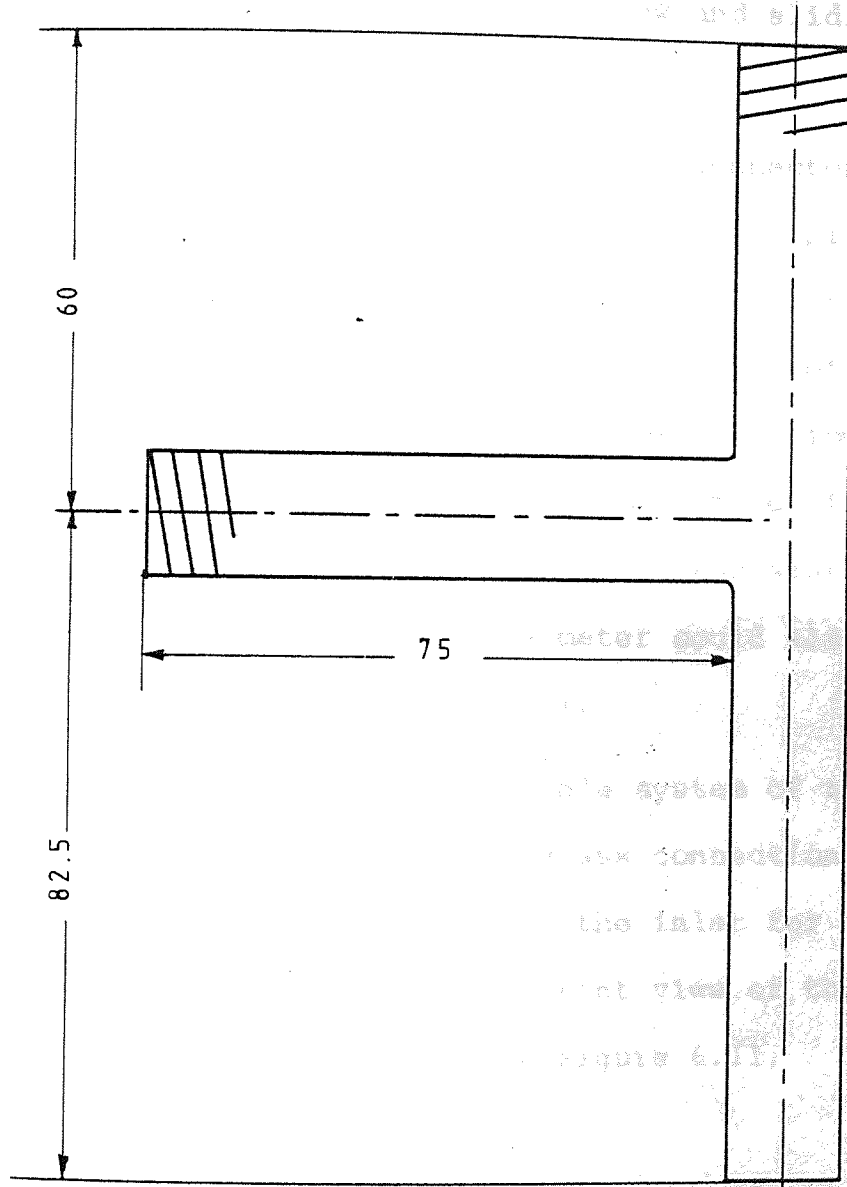


Figure 6.7 bottom section of side arm connector

cabinet. The adjustable weir height, thermocouple setting, downcomer and vent connectors were all achieved with a simple combination of the screw and sliding joints (see Figures 6.8 - 9).

The above setting of the side arm connectors was used for all the plates except the top and bottom plates where a slight adjustment was needed. The inlet of the top plate was modified to a simple sliding joint of S.V.L. 15 for the inflow of the reflux. The lower section of the bottom plate was modified to an L shape made of S.V.L. 15 where the reboiler could be filled for the start-up operation. Connection to a manometer could also be made in this section (see Figure 6.10).

The venting for the adjustable system of the reboiler was achieved through a T shape glass connection made of S.V.L. 15 screw joints providing the inlet for the vapour sampling (see Fig. 6.10). The front view of the completed distillation column is shown in Figure 6.11.

6.2.3 Reboiler

The reboiler was formed from a 225 mm long section of 225 mm I.D. glass tube with a capacity of 0.0065 m^3 and was enclosed at each end by a 6.25 mm thick stainless steel plate. The top plate was connected to a 0.225 m long, 76 mm I.D. glass tube which was connected to the bottom of the lower section of the column. The top stainless steel plate was bolted to the under side of

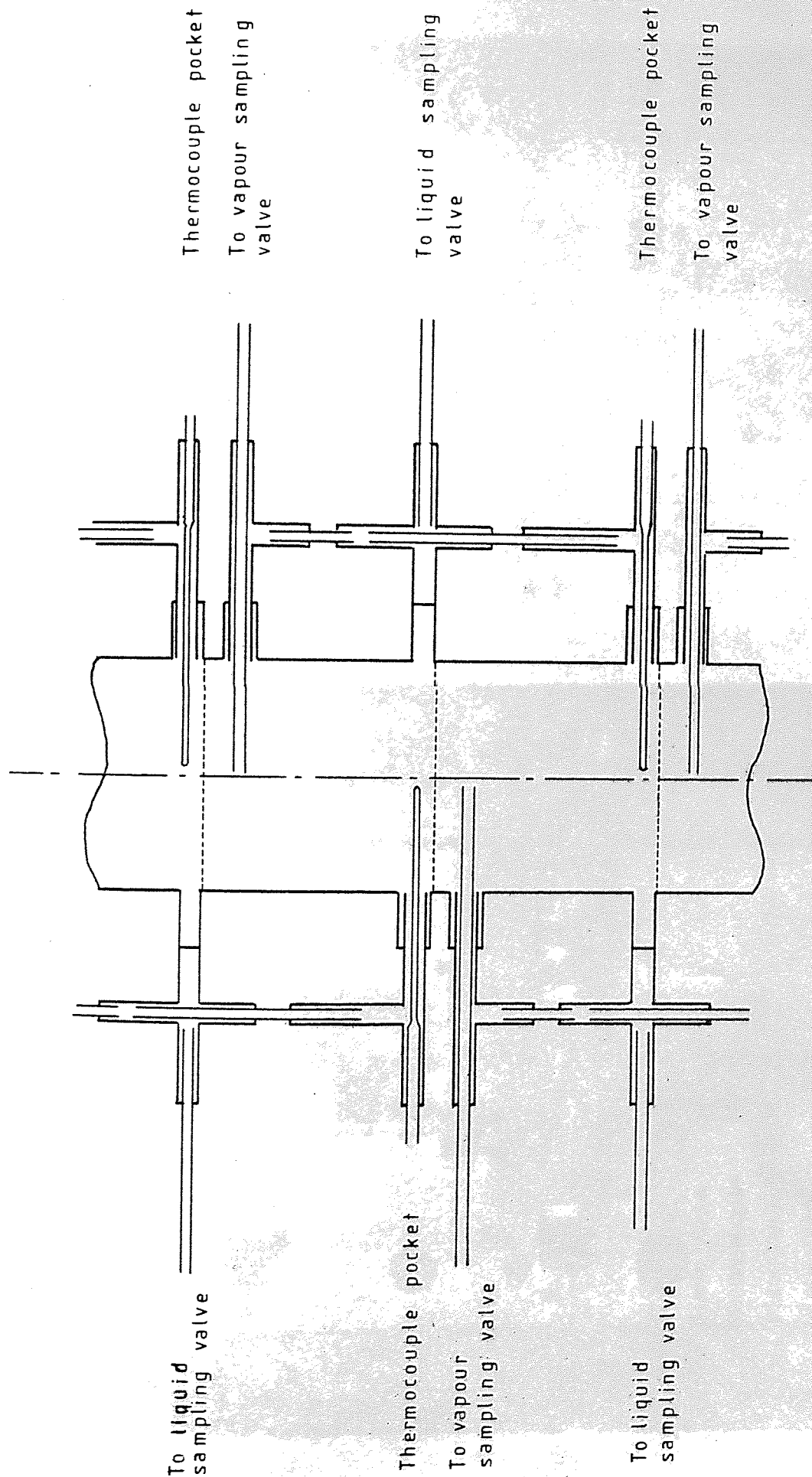
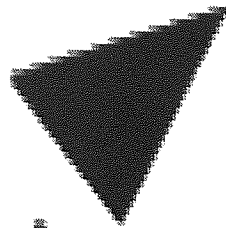
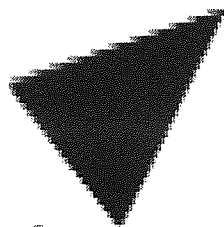


Figure 6.8 side arm connectors assembly



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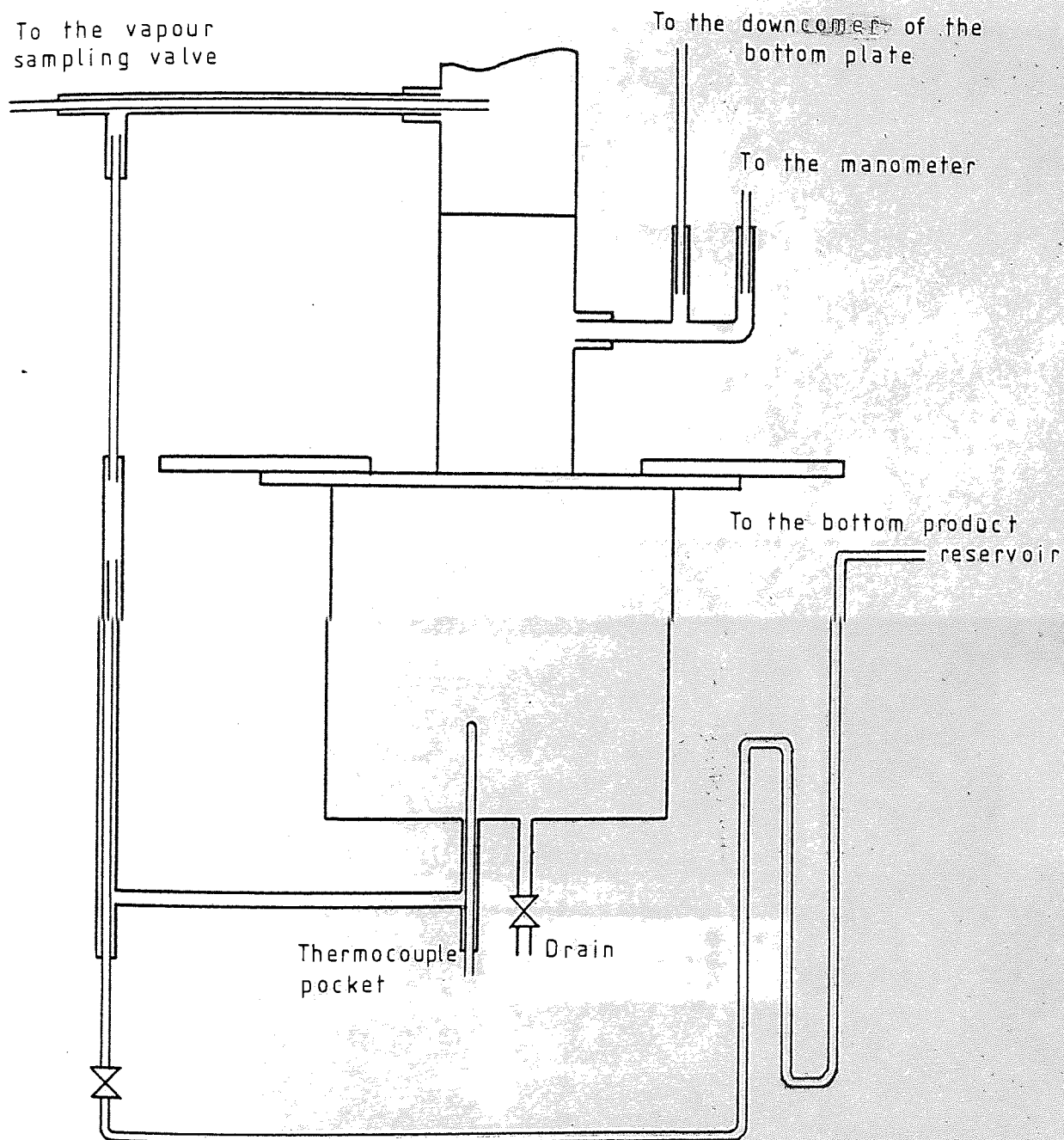
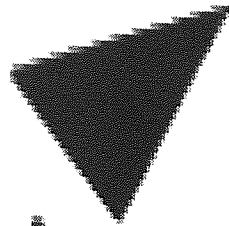
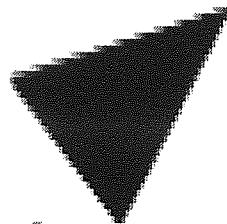


Figure 6.10 diagram of the reboiler



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a 6.25 mm thick mild steel plate using sprung bolts so that expansion and contraction of the column due to the temperature changes could be allowed for. The top of the column was permanently fixed to the surrounding frame work. Two 2 kW stainless steel sheathed immersion heaters were used to supply heat to the reboiler and each element had a 0.74 m cut length of nominal 9.3 mm diameter. A total liquid depth of 100 mm was required to immerse the heaters and this is equivalent to a hold up of 0.004 m^3 . The heat output from one of the heaters could be controlled between 0 and 2 kW by the use of a variable transformer whilst the other heater was used on an on and off basis.

Adjustable hold-up of the reboiler was achieved by a T shape section made of S.V.L. 15 screw joints. The venting of the downcomer to the lower section of the column was achieved through the top arm of the T section. The middle arm was connected to the stainless steel plate at the bottom of the reboiler through a T shape S.V.L. 15 section. The other arm of the T section was used to introduce an 8 mm O.D. thermocouple pocket into the boiler section.

A glass valve attached to a U-shape glass tube was used as a steam trap to prevent the flow of vapour out of the system (see Figure 6.10).

6.2.4 Condenser and Reflux Divider

The condenser was made of 50 mm diameter, 600 mm long glass tube and was lagged with asbestos rope. The column

vapour offtake was similarly lagged. The rate of coolant water was measured by a rotameter (metric size 14), and was controlled with a valve whilst the inlet and outlet temperatures were measured by chrome alumel thermocouples.

The reflux divider was also constructed from glass. Liquid reflux flowed down through the S.V.L. 15 connection, onto the ball and socket valve (89). When the valve was shut, the liquid flowed over the rim of the valve down through the line as reflux to the column. However when the solenoid was activated, causing the valve stem to be lifted and open the valve, the liquid flowed down through the middle of a Q.V.F. (PS07) connection to the top product reservoir.

The valve stem was made from glass tubing to reduce its weight and the seal between the ground glass ball and socket joint was reduced to 2 mm in order to reduce liquid surface tension effects. A ferrite rod was sealed into the top of the valve stem. The whole of the valve assembly was contained inside a glass flask. The solenoid was controlled by a reflux ratio timer which could be adjusted to give a reflux ratio varying between 1:50 and 50:1 (see Figure 6.12).

6.2.5 Feed System

The feed was stored in a 0.1 m^3 aspirator and the reservoir was filled by pumping the feed from an auxiliary 0.1 m^3 reservoir. The feed flowed under gravity through

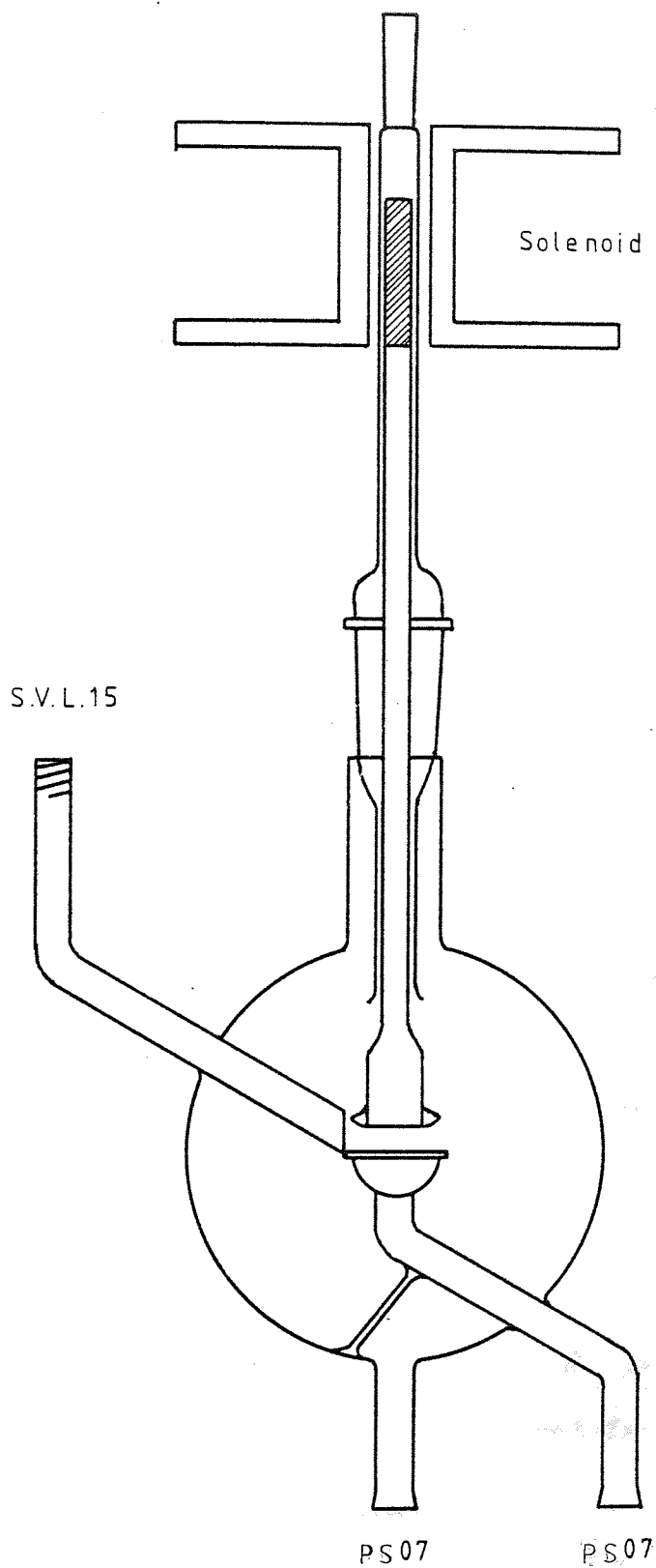


Figure 6.12 reflux divider

glass tubing to a 0-12 scale Fischer and Porter flowrator with a stainless steel float. A glass valve was used for regulating the flow of the feed.

The feed flowed to the feed heater which was constructed from 25 mm diameter glass tube and contained a 0.4 kW electric immersion heater. The heat output from the immersion heater could be varied between 0-0.4 kW by the use of a variable transformer. The temperature of the hot feed was measured by a chrome alumel thermocouple. The inlet and outlet arms of the feed heater were constructed from the S.V.L. 15 screw joints with sliding connections. The outlet of the feed heater was connected to a special feed side arm connector having S.V.L. 15 screw joints on either side as shown in Figure 6.13. The feed heater was clamped to a 5 mm diameter steel bar at the back of the cabinet which served as a stand for the sliding clamp. The feed heater was then positioned in front of the desired feed plate. The lower side arm connector was replaced by the feed side arm connector and an 8 mm diameter glass tube connected the feed heater to the plate through two sliding joints. The feed heater arrangement is shown in Figure 6.14.

6.2.6 Temperature Measurements

Stainless steel sheathed, chrome alumel thermocouples were used to measure all the temperatures. The thermocouples were connected to a common cold junction which was formed from an identical thermocouple placed in crushed

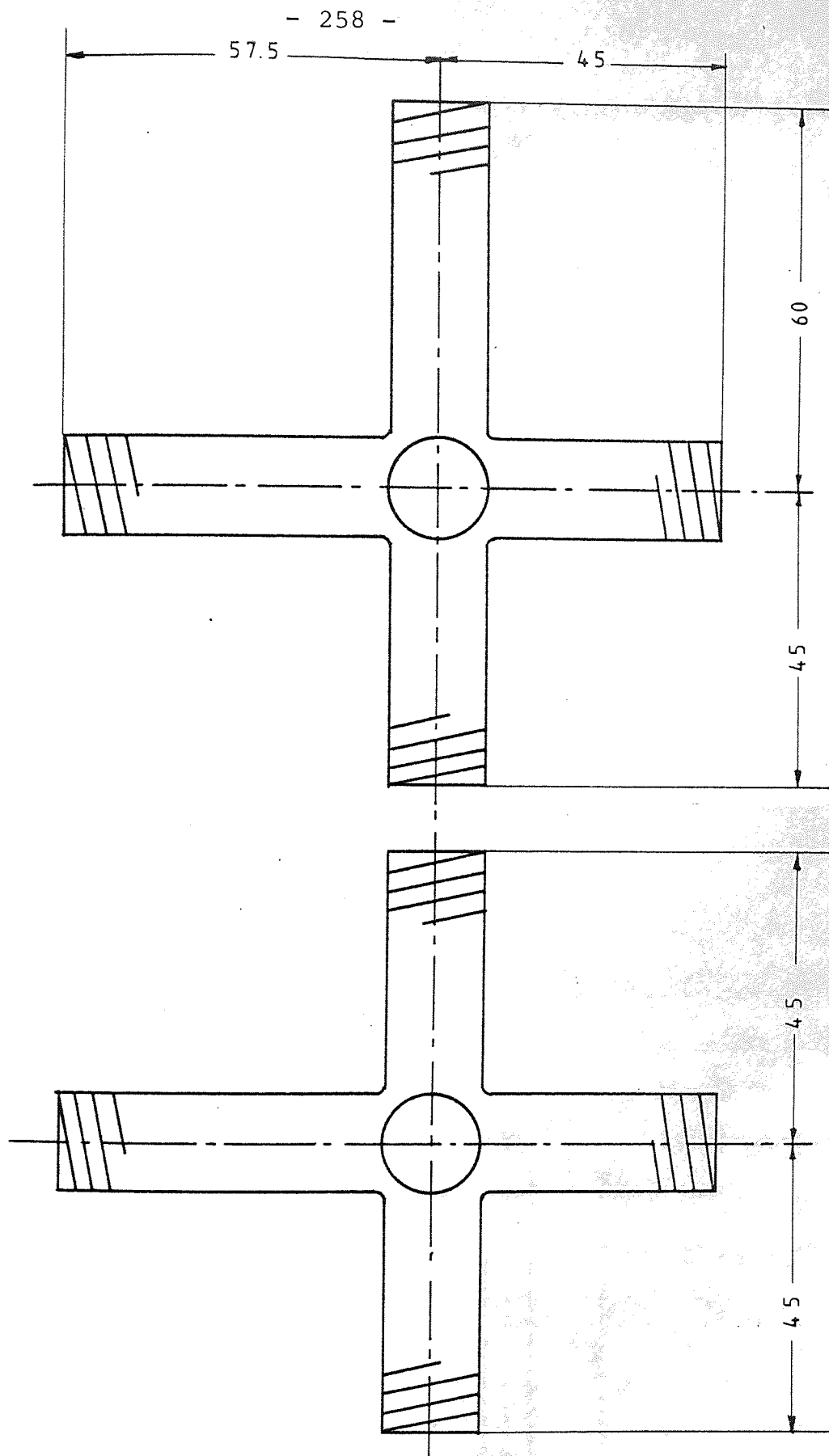


Figure 6.13 feed section of the side arm connector

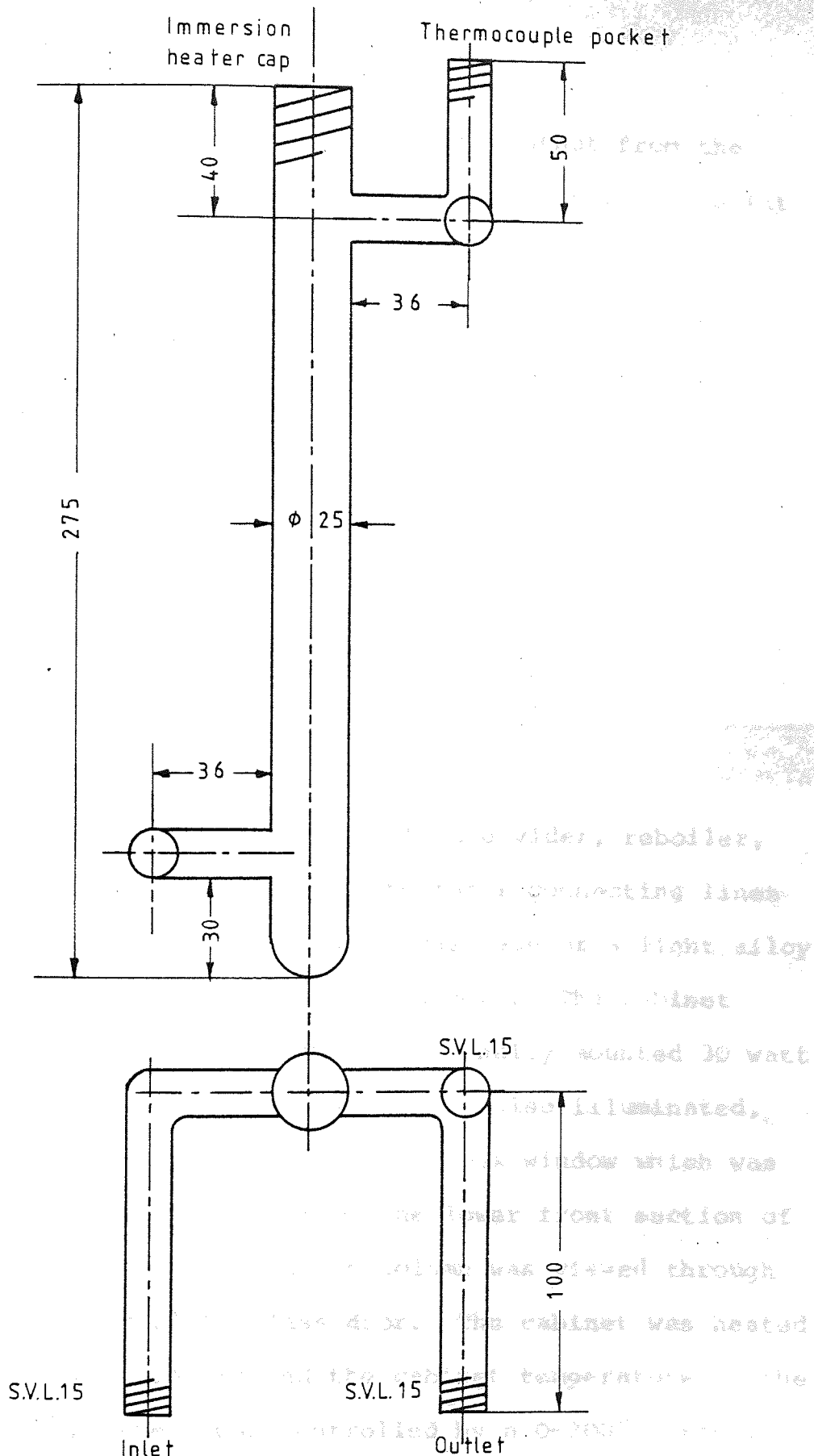


Figure 6.14 the feed heater

ice contained in a Dewar flask. The output from the thermocouples was recorded on a Kent 0-6 M.V., 12 point recorder.

The thermocouples measuring the temperature of the vapour leaving the column and top plate were joined by a two-way switch to terminal 9 and the inlet and outlet cooling water thermocouples were joined by a two-way switch to terminal 12 so that either of the thermocouples output could be monitored at any given time. A complete printout was given every two minutes by the recorder. The terminal number for each thermocouple is given in Table 6.1.

6.2.7 The Cabinet

The distillation column, reflux divider, reboiler, feed heater and all the immediate inter-connecting lines were enclosed in a cabinet which was made of a light alloy framework and asbestos composite sheets. The cabinet interior was illuminated by two externally mounted 30 watt strip lights. The reboiler which was also illuminated, could be viewed through a small perspex window which was mounted on a removable door on the lower front section of the cabinet. The distillation column was viewed through a 9 mm toughened plate glass door. The cabinet was heated by two 3 kW fan heaters and the cabinet temperature in the reboiler compartment was controlled by a 0-200°C thermo-regulator which was connected by a relay system to the fan heaters. The thermo-regulator was set at 100°C. The

cabinet was connected to a fume extraction unit through a 150 mm diameter plastic flexible tube in order to minimise leakage of fumes into the laboratory.

6.2.8 Electrical Circuits

A three-phase 440 volts supply was split into three single phases of 240 volts with a common neutral. The permanent fan heater was connected to the first phase, the reboiler immersion heaters were connected across the second and the variable fan heater and feed heater across the third phase. A voltmeter and ammeter were connected across each of the immersion heaters and the feed heater so that the power input for each heater could be calculated.

The remainder of the electrical equipment was divided equally amongst the phases. Each phase and sub-circuit was fused and fixed with a neon warning light whilst each sub-circuit could be independently isolated.

The electrical instruments were all mounted on a 1.5 m by 1.35 m wooden panel, adjoining the front right hand side of the cabinet. The remaining instruments, feed flowrator, condenser rotameter and manometers, were all mounted on a 0.6 m by 0.9 m wooden panel adjoining the front left hand side of the cabinet.

6.3 CHROMATOGRAPHIC ANALYSIS OF FORMALDEHYDE SOLUTIONS

Following the discussion in Chapter 2, gas chromatography was selected for the analysis of formaldehyde solutions giving a quick and accurate analytical method.

A Pye 104 series gas chromatograph (164) with a Katharometer detector head was used for the analysis. PORAPAK T (240) was used as the packing material in two stainless steel columns with helium as the carrier gas.

The carrier gas flowrate was controlled by the helium gas regulator on the gas cylinder and a needle valve on the apparatus. The flowrate of the gas was measured with a bubble flowmeter.

The constant temperature oven was controlled by a temperature programming unit. The signal from the detector was relayed to an X-Y recorder and a digital integrator. The specification of the equipment is given in Appendix XI.

PORAPAK T with a mesh size of 80/100 was contained in 1.5 m long and 3 mm I.D. stainless steel tubes. The columns were conditioned by purging with helium gas for 24 hours at a temperature of 180°C.

High purity helium gas was used to prevent base line drift and recorder pen fluctuation and the specification is listed in Appendix XI.

The operation procedure of the chromatograph can be found in the Pye 104 series manufacturers manual (164). However, the optimum operating conditions were found by varying the parameters of the chromatograph in the preliminary experiment. (See Appendix XI.1).

The samples were injected into the chromatograph using a Hamilton 7001 N precision syringe with a Chaney Adaptor. The samples were 1 mm^3 for both the condensed vapour and liquid.

The calibration procedure, graphs and specification of the items are given in Appendix XI.

6.4 OPERATION OF THE DISTILLATION COLUMN

After the required conditions for the specified variables were established in the planning of the experiments, the feed position, weir height, feed flowrate, reflux ratio, constant water flowrate and heat input to the boiler could be set in the distillation column.

The fan heaters were first switched on and two hours was allowed for heating the cabinet. The feed was pumped to the feed tank and all the air from the connecting lines was expelled through the venting valves. The reboiler was filled with a formaldehyde solution similar to the composition of the feed. The immersion heaters were switched on and the column was operated at total reflux allowing the concentration and temperature profile to develop in the column. Steady state for the total reflux was reached within approximately 1.5 hours. The feed and the feed heater were switched on and the feed was allowed to flow onto the feed plate. The reflux divider was activated and the top and bottom products were collected in containers. Boiling of the feed in the feed heater was avoided in-

order to reduce fluctuations in the feed flow lines. The feed was heated to approximately 5°C below its boiling point.

The heat input to the reboiler was adjusted to prevent flooding of the column and weeping of the liquid from the plates. The feed flowrate, feed heater energy input and the coolant water were all checked and adjusted to the required rates. The ammeters, voltmeters, column pressure drop, feed flowrate and condenser water flowrate were all constantly checked until steady state had been achieved.

Steady state condition was reached in approximately 2 hours. This condition could be observed from the constant temperature readings from the temperature recorder. This was checked in preliminary experiments by analysing the liquid samples from the column at twenty minute time intervals. The average difference between the samples was less than 2 percent. Therefore the constant reading of the temperature recorder was assumed to give an accurate indication of the steady state condition in the column.

The column was allowed to operate for another two hours before samples were taken. The flowrates of the top and bottom products were taken in ten minute intervals by measuring the volume and weight of the samples over a known time period. Approximately 9 to 10 readings were taken for each product flowrate. The temperatures, ammeters, voltmeters, column pressure drop and the flowrates of the feed and cooling water were constantly checked

ensuring that these values did not change in the operation.

The liquid and vapour samples were collected. The liquid samples were taken in the sampling bottles through the liquid sampling valves. Before taking the liquid samples, about $5,000 \text{ mm}^3$ of liquid was withdrawn and returned to the storage bottles. This was done to drain the stagnant liquid in the connection tubes. The vapour samples were condensed in sampling bottles, jacketed with ice. These samples were taken through three way glass valves. The valve was turned to first position allowing the vapour to flush and drive all the condensate from the sampling tube into a condensation chamber, which later was returned to the storage bottles. The valve was then turned to the second position where the vapour condensed in the sampling bottles. The plate temperature was checked after each sample was taken. Immediately before and after sampling, the parameters which were outlined earlier were all measured.

At the end of the experiments the feed was stopped, and all the electrical units were switched off. The cooling water was allowed to flow through the condenser for cooling. When the column was cooled the top and bottom products were collected and mixed with the remainder of the feed and returned to the storage bottles. After every five experiments fresh formaldehyde solution was used for the new experiments, since the composition of the solution

may have been altered by the escape of the more volatile components from the top of the condenser.

6.5 THE PLANNING OF THE EXPERIMENTS

The objective of collecting the experimental data for the distillation of formaldehyde solution in a sieve plate distillation column, was to establish a measure of the performance of the mathematical model. Thus a number of experiments at different conditions were required. However, the experiments were not aimed at a complete cover over the whole experimental possibilities.

The main parameters which could be investigated are listed in Table 6.2. However the operating range was found to be limited by the system behaviour. These constraints are discussed in detail in Chapter 7.

Considering the items in Table 6.2, the parameters could be monitored as follows. The feed rate could be varied with a glass valve located in the feed line before the feed flowrator. The feed composition could be adjusted by adding ANALAR grade methanol or distilled water to the original feed. The feed plate position could be varied by sliding the feed heater to the appropriate position and connecting the feed heater to the lower section of the side arm connectors. The plate hold-ups could be changed by sliding the 8 mm diameter glass tube in the lower arm of the middle section of side arm connectors, giving different weir height. The reboiler

hold-up could also be varied in the same way as the hold-up of a single plate could be varied. The boil-up rate was controlled by varying the electrical supply to one of the immersion heaters. The reflux ratio was controlled by adjusting the setting on the timer control section of the solenoid valve. The condensation rate could be controlled by monitoring the cooling water flowrate.

Considering the limitations that the formaldehyde solution imposed on the above mentioned parameters, as explained in Chapter 7, the experiments were carried out as follows.

The experiments were divided into 5 groups where the feed plate position was varied from stage 8 to stage 4. In each of these groups, the reflux ratio was varied from 5:1, 10:1, 20:1 to total reflux. Five more experiments were carried out with stage 8 as the feed plate and a reflux ratio of 10:1 varying the composition of the feed. The planning of the experiments was a function of several constraints due to the behaviour of the formaldehyde solutions. The constraints and factors which are involved in the experiments are discussed in Section 7.6. The list of experiments and operation parameters can be found in Appendix XII.3.

Table 6.1
Temperature Readings

TERMINAL NO.	LOCATION
1	Boiler
2	Plate 1
3	Plate 2
4	Plate 3
5	Plate 4
6	Plate 5
7	Plate 6
8	Plate 7
9A	Plate 8
9B	Vapour exit
10	Reflux
11	Hot feed
12A	Cooling water out
12B	Cooling water in

Table 6.2
Operation Parameters

1. The feed rate
2. The feed composition
3. The feed plate position
4. The plate hold-up
5. The reboiler hold-up
6. The boil-up rate
7. The reflux ratio
8. The condensation rate

CHAPTER 7

DISCUSSION AND CONCLUSIONS

The results obtained by the
analysis of the products of the
reaction of furfuraldehyde with
methanol under the conditions imposed
by the pressure and
temperature are in the state of furfuraldehyde
which has already been mentioned
in the literature. The results
obtained suggest that the
reaction of furfuraldehyde with
methanol and water in the presence of
acid. Methylethyl glycol is produced in the reaction.

7. DISCUSSION AND CONCLUSIONS

7.1 STATE OF FORMALDEHYDE IN THE SOLUTION

The study of the physical properties of formaldehyde has revealed that formaldehyde is a highly volatile gas at the boiling temperature of aqueous or alcoholic solutions. A large concentration of formaldehyde can not be found in the free state because of the considerable difference between the boiling point of pure formaldehyde and the average boiling point of the solution (about 100°C at atmospheric pressure for a wide concentration range). Furthermore, it is thought that as there is a comparatively large formaldehyde content in the liquid phase, the formaldehyde is present in the form of a heavy and less volatile component.

The volatility of formaldehyde is changed by the addition of methanol to the aqueous solution of formaldehyde, suggesting that a new form of formaldehyde is present in the solution. Also formaldehyde is decomposed to formic acid and methanol as the system pressure and temperature are increased.

Several investigations into the state of formaldehyde in methanol or water solutions have already been mentioned in Chapter 2 and the reasons for the unusual behaviour of formaldehyde solutions have been suggested. It was concluded that formaldehyde exists in chemical equilibrium with both the water and methanol in the vapour and liquid phases. Methylene glycol is produced from the reaction

of formaldehyde and water and heavier polymers of formaldehyde are formed in the later stages of the reaction. It can be shown from the equilibrium constants of these reactions that the equilibrium of formaldehyde with methylene glycol is achieved very quickly. However, the formation of the polymers has been found to be very slow (41). The polymerisation reaction is slowed by an increase in temperature. It was therefore assumed that methylene glycol is the only significant reaction product because of the very low concentration of formaldehyde polymers normally obtained at atmospheric distillation temperatures.

Hemiformal is produced as the first product of the reaction between formaldehyde and methanol whilst hemiacetals and heavier polymers of formaldehyde are produced in the later stages of the reaction. The reaction of formaldehyde with methanol has also been found to be very fast (41). However, the hemiacetals are produced slowly (41) and unlike hemiformals have been found to be stable chemical compounds. The heavier polymers are assumed to be negligible since the concentration of free formaldehyde will be further reduced by the reaction of formaldehyde with methanol. Furthermore, the concentration of the polymers will be reduced by the relatively high boiling temperatures of the solution (70 to 101°C.) at atmospheric pressure.

Decomposition of formaldehyde due to temperature

and pressure can be assumed to be negligible as atmospheric pressure is not high enough to cause any decomposition.

Hemiformal and methylene glycol are known to be unstable compounds and to only exist in chemical equilibrium. These components have not yet been isolated in the pure form.

The significant reactions occurring in the distillation column have been assumed to be the chemical equilibrium of formaldehyde with methanol and water producing hemiformal and methylene glycol respectively. The validity of these assumptions was demonstrated in the experiments as no precipitation of the formaldehyde polymers was observed in the distillation column and no trace of the hemiacetal was obtained in the chromatographic analysis of the samples. Also, formaldehyde was assumed to be a non-condensable gas at the distillation temperatures, as the critical temperature of formaldehyde was just higher than the boiling point of the solutions. Alternatively, the free formaldehyde in the liquid phase was considered to be dissolved gas in a liquid.

7.2 ANALYSIS OF FORMALDEHYDE

Gas chromatography was employed for the quantitative analysis of formaldehyde because of the fast and accurate response which can be obtained using this method.

Accurate results for the quantitative analysis of the chromatograms can be obtained using peak areas rather than

peak heights. The peak areas in this work were obtained using an electronic digital integrator linked to the chromatograph.

A Hamilton (7001 N series) precision syringe with a chaney adaptor with a reproducibility of less than ± 1 percent was used for the injection of all the samples. As the same syringe and same sample size were used throughout the experiments, the accuracy of the analytical results was not affected by the syringe except in the reproducibility. However, the accuracy of the syringe was less than ± 2 percent.

Several standard samples of formaldehyde-methanol-water and methanol-water were repeatedly analysed on the chromatograph. A maximum error of ± 0.8 percent was obtained from the comparison of the results from the chromatograph with the concentrations of the standard samples. However, a larger error of ± 4.0 percent was obtained for very low formaldehyde concentration (less than 0.007 mole fraction). Although the percentage error might be large, the absolute error which is the difference between the concentration in the standard solution and the concentration obtained from the chromatograph, is very small. Nevertheless, the calculations for ^{the} distillation column are not affected in any way since in all of the experiments the concentration of formaldehyde in the bottom product was always larger than

0.007 mole fraction.

After every ten experiments, the response of the chromatograph was checked by injecting a standard sample and comparing the actual and calculated results. No change in the response of the chromatograph was observed.

The magnitude of the error in the analysis of the samples was well within the accuracy of the mathematical model and therefore a constraint on the final results was not imposed by the analytical result.

7.3 VAPOUR-LIQUID EQUILIBRIUM OF FORMALDEHYDE SOLUTIONS

Thermodynamic relationships expressing the vapour-liquid equilibrium of the chemically reacting systems were developed by combining the relationships expressing the phase and chemical equilibria. The phase equilibria relationships were based on the equality of the fugacities in the liquid and vapour phases where the fugacity of the phases were expressed as a function of the physically real parameters. The equations defining the chemical reaction were based on the mechanism of the reactions.

The liquid and vapour models were defined in order to relate the fugacity of each phase to the physically real parameters. The virial equation of state was used to relate the pressure and temperature and volume of the vapour phase. The fugacity coefficients were defined by a rigorous thermodynamic relationship. The Wilson equation was used to define the activity coefficients

as described in Chapter 3. The Wilson parameters were then estimated from the available experimental X, Y, P and T data.

The formaldehyde-water and formaldehyde-methanol-water systems were analysed into the constituent binary systems for the purpose of the calculations. Some of the resulting binary systems were found to be hypothetical systems and these systems were defined only for calculation purposes. Such binary systems cannot be isolated as a third component is immediately produced in the resulting chemical reaction.

Formaldehyde was first treated as an ordinary condensable component and the calculations were performed for the resulting systems. However, a considerable improvement in the calculated results was achieved by assuming that formaldehyde acts as a non-condensable component. Therefore, the results reported in this work are based on the assumptions that formaldehyde be treated as a non-condensable component.

The Henry's constant and Wilson single energy parameter were used to define the binaries which included the non-condensable component. The Wilson single parameter equation was used because the significance of the non-condensable parameter was reduced by the low concentration of formaldehyde in the liquid phase.

In order to reduce the number of parameters to be estimated in the quinary system, the parameters for the

ternary system were first estimated and then used as the given values in the estimation of the remaining parameters in the quinary system. The parameters were estimated by minimising the difference between the calculated and experimental pressure. During the calculation, it was found that the program was unable to estimate the Henry's constants. The Henry's constants could not be estimated during the optimisation of the pressure function when the derivatives of the function with respect to the Henry's constant were almost equal to zero and thus no further improvement of the function could be achieved by changing the value of the parameter. In estimating the parameters for the non-condensable formaldehyde, a very large value (465.672 kJ/mol) was obtained for the Wilson's energy parameter for the binary system of formaldehyde and the reference component, water (see Appendix XIV). From this large positive value, a very small Wilson parameter was calculated which resulted in a very low activity coefficient of almost zero for free formaldehyde. The liquid phase fugacity was thus caused to be almost zero. Detectable improvements in the calculated vapour phase concentration and consequently in the calculated pressure were not achieved from the minor variations in the Henry's constant which is equal to the standard state fugacity. These values were therefore estimated using simplifying assumptions (see Appendix XIV).

However, despite complications and difficulties, acceptable

results with good accuracy were produced from the proposed model for the phase equilibria of the chemically reacting system of formaldehyde-methanol-water.

The results from program BUBLDILF for the quinary system were compared with the available experimental data and good accuracy was obtained except for the region of 0.01 to 0.12 mole-fraction liquid methanol (see Table XIII.1). It was found that in this low methanol concentration region, the calculated methanol vapour mole fractions were lower than the experimental values and the calculated values for the formaldehyde vapour mole fractions were higher than the experimental formaldehyde content. However, the maximum error was found to be less than 0.09 mole fraction. Similarly the calculated temperature was lower than the experimental temperature. The concentration and temperature were corrected by fitting a polynomial to the difference between the calculated and experimental values (see Appendix XIII).

Although the problem was solved, the method lacked the theoretical consistency in the low methanol concentration region. The lower accuracy in this concentration region was thought to be caused by -

- (a) a change in the reaction mechanism, which may cause variation in the form of chemical reaction equilibrium constants,
- (b) the presence of another reaction which is not accounted

for in the model, which may produce new components into the system.

- (c) inaccuracies caused by extrapolation of the reaction constants, which may produce errors in the calculated true mole fractions.
- (d) inaccuracies caused by calculating the physical properties from generalised estimation techniques, which represents error in the calculation of thermodynamic properties.

The lack of accuracy in the low methanol concentration interval could have been caused by any of the above factors. This problem could be overcome by obtaining more information about the reaction of formaldehyde with water or methanol and the appropriate physical properties. The problem could also be solved by estimation of a new set of parameters for this concentration region which may cause discontinuity in the calculated results.

7.4 DISTILLATION CALCULATIONS

Two main sections are used in the mathematical model of the distillation column, the phase equilibria calculations and the mathematical relationships defining the distillation process. Each of these sections and the various methods for the solution of these sections have been discussed in Chapters 3 and 4.

The results from the mathematical model were compared with those obtained from the operation of the actual

distillation column. The mathematical model was developed in a general form in order to produce results under similar conditions to those of the experiments. The solution of the mathematical model was achieved by setting the experimental parameters and defining a number of other specified parameters such as the feed rate, reflux ratio, bottom product flowrate and composition.

In solving the distillation process with the proposed model, the simultaneous solution of equations was first tried but no convergence was achieved. The tray to tray method of solution with minor simplification in the tray model was applied, where convergence of the problem depended on the convergence of the solution for each plate and the convergence of the temperatures throughout the column.

In the simultaneous method of solution, the model for the tray was comprised of an ordinary distillation tray with two chemical reactors for the effluent vapour and liquid phases. Mass transfer of the components was achieved in the distillation tray section where the resulting vapour and liquid phases had concentrations which were different from the equilibrium values. Equilibrium was reached in each phase in the proposed vapour and liquid phase chemical reactors.

The components leaving the chemical reactors were assumed to be in chemical equilibrium because of the very fast rate of reaction and the high temperatures of the distillation tray. This assumption can further be

justified since the columns distilling the formaldehyde solutions operate with low boil-up rate to avoid flooding of the column which results in longer residence times for the liquid and vapour phases on each tray. Thus the significant reactions which need fractions of a second to complete can reach the equilibrium in the available residence time.

The simultaneous method of solution was found to be highly unstable and after three or four iterations the solution had diverged to cause negative concentration and temperature values which in turn gave meaningless values in the phase and chemical equilibria routines. Although several combinations of mass and energy balance equations were tried, no improvement was achieved in the method of solution.

The divergence of the solution is thought to be caused by an inadequate representation of the tray efficiencies and also by the effect of the chemical reaction. The number of reacted moles calculated for each tray differed greatly from the actual values at the early iterations. The calculated values of liquid phase mole fractions were found to be very sensitive to the number of reacted moles. A slight variation in the number of reacted moles was found to cause a large deviation in the estimated liquid mole fractions. Therefore, convergence could not be achieved unless a very accurate estimate of the reacted number of moles was available as the initial guess for

the parameters. However the number of reacted moles could not be accurately estimated without performing the actual calculations and a further complication has been introduced. Therefore the model for the distillation process was simplified and a tray to tray method of solution was applied. In this method, each tray could individually be studied and the effect of each parameter could be investigated for the convergence of that particular tray.

The tray model was simplified by assuming that the vapour phase leaving the tray was already in chemical equilibrium. The tray model was reduced to a mass transfer section and a liquid phase reactor by the implementation of this assumption. A detailed explanation of this assumption can be found in Chapter 4. Thus the chemical reaction is effectively removed from the vapour phase to the liquid phase.

The calculated vapour or liquid phase concentrations are not changed by this assumption from that of the actual values. However, the calculated number of reacted moles is not found to be equivalent to that of the actual reacted moles in the vapour or liquid phases. As only the values of the vapour and liquid phase concentrations were of interest, this method was used for the distillation calculations (see Section 4.3.2).

The distillation calculations are affected by the plate efficiency. Originally it was intended to obtain experimental Murphree efficiencies for each component.

However the vapour phase compositions could not accurately be measured with the available equipment. Therefore estimation techniques based on the A.I.Ch.E. method (133) were used for the plate efficiency calculations.

Values of the plate efficiency calculated from the A.I.Ch.E. method were found to provide an average representation for the column efficiency. However the values for each component were found to be lower or higher than the actual values depending on the position of the feed plate.

The calculated efficiency values were modified for one experiment with a set feed plate position. The actual efficiency for each component on a plate was evaluated by trial and error. The modified values were applied to the other experiments with the same feed plate position and good agreement was obtained.

The calculated efficiency values were found to be lower than the actual values for plates above the feed plate and higher for the plates below the feed plate when the feed plate was located at stages 7 and 8. The calculated values were found to be higher for both the plates below or above the feed plate when the feed plate was located at stage 6. The calculated values were lower for the plates below the feed plate and higher for the plates above the feed plate when the feed plate was located at stages 4 and 5.

The discrepancy is thought to be caused by a number

of reasons:

- (1) inaccuracy of A.I.Ch.E. method for small scale the columns,
- (2) the effect of chemical reaction which is not considered in the A.I.Ch.E. method,
- (3) lack of accurate physical property data,
- (4) inaccuracy of the A.I.Ch.E. method in predicting the efficiency for multicomponent systems.

A linear relationship was derived for calculating the difference as a function of feed plate position for both the plates below and above the feed plate in the form of equation 7.1 for the plates below the feed plate and equation 7.2 for the plates above the feed plate. The values of ΔE_1 and ΔE_2 are simply added to the calculated efficiency values to obtain the actual efficiency.

$$\Delta E_1 = A \quad (7.1)$$

$$\Delta E_2 = B \times (N - N_F) + C \quad (7.2)$$

The values of A, B and C were found to be the same for feed stages of 7-8 and 4-5. The calculated values of the efficiency for the total reflux was found to be lower than the actual values. The constants in equations 7.1 and 7.2 are listed in Table 7.1.

The efficiency of the reboiler was defined by equation 7.3

$$EB = \frac{Y_{R1,i} - X_{R1,i}}{Y_{R1,i} - X_{R1,i}} \quad (7.3)$$

where XR_1 , YR_1 and YR_1^* represent the mole fractions of the liquid leaving the reboiler, the vapour leaving the reboiler and the vapour in equilibrium with the liquid leaving the reboiler respectively. The subscript i represents the components from 1 to 5.

The efficiency for the reboiler was estimated by trial and error, comparing the calculated and experimental results. The value of EB was found to be 0.4 for all the experiments.

Table 7.1

Feed plate location	A	B	C
7-8	- 0.65	- 0.15	0.9
6	- 0.65	0.0	- 0.15
4-5	0.5	0.0	- 0.75
Total reflux	0.65	0.0	0.0

7.5 SOLUTION OF MATHEMATICAL MODELS

The thermodynamic relationships representing the phase and chemical equilibria were solved numerically by the computer programs. The bubble temperature technique of solution was used where the mole fraction of the vapour phase and the equilibrium temperature are calculated knowing the liquid phase mole fraction and the system pressure. The evaluation of the activity

coefficients, the liquid partial molar volume, the vapour phase fugacity coefficients and second virial coefficients were obtained in the calculation. Different subroutines were assigned for the computation of each of these items together with the programs for the phase and chemical equilibria.

In order to use these programs, several binary parameters had to be estimated using optimisation techniques. Furthermore, some physical property data of the pure components were needed in both the equilibrium and parameter estimation sections. The physical property data were either estimated using the appropriate generalised techniques or were calculated by computer programs. The constants for the equation representing the vapour pressure as a function of temperature were calculated by program VAPFIT.

Subroutines BMARQ and BSOLVE based on Marquardt's optimisation technique, were used for estimating the parameters. Subroutines EVALU and CALPLW were used for co-ordinating between the parameter estimation and phase equilibria calculations. COMP5 was set as the main segment for the program.

The programs for the phase and chemical equilibria calculations can be applied to both the formaldehyde-methylene glycol-water system and the formaldehyde-hemiformal-methanol-methylene glycol-water system with some minor

modifications. The calculation technique used in the parameter estimation, phase and chemical equilibria calculations can be applied to any reacting system provided that the mechanism of the reaction is known and sufficient physical property data and experimental data are available.

The solution of the multicomponent distillation problem was achieved by combining phase and chemical equilibria section with the solution of the distillation process. The subroutines for the phase and chemical equilibria calculations were utilised with the following subroutines.

The set of simultaneous nonlinear equations to be solved by subroutine GAUSS was linearised by subroutine NEWTON. Subroutine EFFICIENCY was used to calculate the efficiency of the sieve plates in the distillation column. The main segment of distillation programs was entitled CHEMICOL.

The results from the computer programs will be therefore discussed in Section 8 of this chapter.

7.6 EXPERIMENTS AND APPARATUS

Several parameters can be adjusted independently to change the conditions under which the column could be operated. The following parameters could be changed : the feed plate position, the feed flowrate, the plate and reboiler hold-up, the reflux ratio, the condenser cooling

water flowrate and the reboiler heat input.

It was intended to vary all the adjustable parameters. However, the magnitude of some of the parameters was severely limited by the physical behaviour of the system.

The tendency of the system to foam on the distillation plates and in the reboiler was found to be a major constraint and if the heat input to the column was increased, the column was immediately filled with foam.

In distillation the surface tension of the components can be used to give a measure of the tendency of the system to foam. In order to include the effect of weeping and entrainment, some empirical equations should be included in the relationships defining the plate efficiency values. This in effect would result in increased inaccuracies by complicating the relationships for calculation of plate efficiencies. Furthermore, since the extra relationships are in terms of physical properties which are not reported for formaldehyde, hemiformal and methylene glycol, the possibility of larger errors will be increased. Therefore it was decided to try to avoid foaming, flooding, weeping and entrainment in the column by careful control of the heat input in the reboiler. This was achieved by visual observation of the distillation column under the operation. Therefore the boil-up rate could not be varied independently.

Similarly, the plate hold-up was affected by the tendency of the system to foam. As the boil-up rate was low, large

hold-ups would cause weeping effects on the sieve plate and very low hold-ups would cause vapour channelling through the liquid. In order to avoid weeping and vapour channelling, the weir heights could only be varied between 26 to 41 mm. No entrainment was observed because the column would have been flooded before the boil-up rate was sufficiently high to cause entrainment.

Local deficiencies (see Section 2.4) as noted by Olsson and Svensson (73) would be caused by a high boil-up rate. The local deficiencies can be explained by considering a formaldehyde solution in which most of the formaldehyde in solution is in the form of methylene glycol or hemiformal. Formaldehyde can be transferred to the vapour phase if sufficient free formaldehyde has been produced by the dissociation of hemiformal and methylene glycol in the liquid phase. Although the amount of formaldehyde transferring to the vapour phase by evaporation of free formaldehyde is negligible compared with that which is produced by the decomposition of methylene glycol in the vapour phase, super heating can be introduced by starvation of the liquid phase of free formaldehyde. This can be further explained by considering the situation where the evaporation of free formaldehyde from the liquid phase is greater than the rate of dissociation of methylene glycol in the liquid phase. A lower formaldehyde concentration would be caused in the liquid phase which in turn would cause superheating in

the liquid and vapour phases. Therefore the distillation column was operated with a maximum hold-up in the reboiler in order to offset the local deficiencies, by having a larger number of moles available for the formation of the free formaldehyde by dissociation of the methylene glycol. The maximum weir height of the reboiler was set to 157.5 mm which is equivalent to a liquid hold-up of $0.6262 \times 10^{-2} \text{ m}^3$.

The feed could only be heated to just below its boiling point in the feed heater as fluctuations in the feed rotameter and pulsations on the feed plate were caused by a boiling liquid feed.

The condenser was operated at maximum capacity to minimise the escape of free formaldehyde from the top of the condenser. Some of the free formaldehyde was lost through the vent on top of the condenser, because of the low boiling point of free formaldehyde. However, it was assumed that the loss was negligible because of the low boil-up rate and low concentration of formaldehyde in the condenser.

Stagnant zones were not observed in the side arms and the connecting tubes on the column. Furthermore, the volume available for the accumulation of stagnant liquid was minimised because of the construction of the sliding joints which consisted of two or three glass tubes inside each other. Liquid or vapour samples were taken from the streams leaving the plate, and these

values could be compared with the values obtained from the mathematical model. Prior to each sampling, the valves and sampling tubes were drained of the condensate, ensuring that representative samples were taken from each stream.

However, for the vapour phase sampling, poor results with poor reproducibility were obtained. Partial condensation of formaldehyde in the condensation chamber was thought to be the major cause of the inaccurate results. The temperature of the condensation chamber could not be lowered further since, even with crushed ice as the coolant, some evidence of polymerisation was observed, especially at the lower plates of the column where the concentration of formaldehyde was higher. The use of freezing techniques was discarded because the rate of polymerisation increases rapidly with a decrease in temperature. Therefore the experimental vapour compositions were not used in the subsequent calculations although the samples were still collected and analysed for all the experiments.

When all the samples had been collected, they were analysed on the gas chromatograph commencing with the bottom plate sample. By following this procedure the occurrence of any undesirable polymerisation reactions was minimised.

In the trial runs, five experiments were carried out under the same conditions. The difference of less than

5 percent was obtained for the concentration and flow-rates in different experiments. However, the reproducibility is well within the accuracy limit of the calculations and therefore no constraint is imposed by the experimental results.

7.7 PHYSICAL PROPERTIES

The physical property data for the components in the quinary system of formaldehyde-hemiformal-methanol-methylene glycol-water were not well reported in the literature. Therefore, the necessary physical property data had to be estimated for formaldehyde, hemiformal and methylene glycol using generalised techniques.

The critical pressure, volume and temperature of the components could be calculated starting from the normal boiling points. The normal boiling points of the components, except hemiformal, are reported in the literature. Meissner's equation (165) was used to calculate this value and the claimed accuracy for the method was reported to be 7 percent (see Appendix V.1).

The critical properties of formaldehyde, hemiformal and methylene glycol were calculated using Eduljee's additive contribution method (165) with an average maximum error of 10 percent (see Appendix V.1).

The molar volume of the liquids at the normal boiling point was calculated (165) with an error of 5 percent. The liquid density could be extrapolated for other

temperatures by utilising Goldhammer's equation (158) with an error of 5 percent (see Appendix V.2).

The partial molar volume of formaldehyde in the other components was calculated from the method presented by Lyckman, Eckert and Prausnitz (242,168) with a claimed accuracy of 2 percent (see Appendix V.4).

The heat capacities of the components in the vapour phase were estimated using Janz's estimation technique (169) with an accuracy of 4 percent (see Appendix V.5).

The heat of vaporisation of hemiformal and methylene glycol were calculated using Watson's equation (169) at the normal boiling point. The evaluated heats of vaporisation were extrapolated to other temperatures using Watson's equation (169) with an average error of 5 percent (see Appendix V.6).

The reaction constants for the equilibrium of formaldehyde and methanol in the liquid phase were estimated using rigorous thermodynamic relationship. The entropy, enthalpy and free energy of the reaction were estimated (169) with an error of less than 5 percent (see Appendix III).

The viscosity of pure liquid formaldehyde, hemiformal and methylene glycol were calculated from Arrhenius's relationship (158).

The viscosity of the solution was then calculated by fitting a polynomial as a function of temperature

and concentration to the data given by Walker (41) with a maximum error of 2 percent (see Appendix IV.1).

The diffusivity of the components in the liquid phase was calculated using the Wilke and Chang's correlation (248) with a maximum error of 10 percent (see Appendix IV.3).

The vapour phase viscosity for the component was calculated (158) with a maximum error of 10 percent. The viscosity of the vapour mixture was calculated from the Wilke's equation (158) (see Appendix IV.2). The diffusivity of each component in the mixture was calculated (158) with the accuracy of 5 percent (see Appendix IV.4).

In the estimation of vapour pressure data for formaldehyde, hemiformal and methylene glycol, the normal vapour pressure estimation techniques were avoided because of the large errors caused by the unusual behaviour of these components. The accuracy of the vapour-liquid equilibrium calculations were dependent on the accuracy of the vapour pressure data. For formaldehyde, the vapour pressure data presented by Walker (41) was used in the program VAPFIT to calculate the constants of the vapour pressure equation.

The vapour pressure data for hemiformal was evaluated by assuming the validity of Raoult's law with ideal liquid and vapour phases. The vapour-liquid equilibrium data (41) was used to calculate the vapour pressure of the component at different temperatures. Although errors

are introduced by utilising Raoult's law, the error was thought to be less than the alternative estimation techniques. The vapour pressure data for methylene glycol was produced from Clausius-Clapeyron equation. The vapour pressure of methylene glycol has been reported by Chueh (220) but these values were found to be reliable only at the boiling point region. Data close to the boiling point were used to estimate the heat of vaporisation as a function of temperature. Substitution of this function into ^{the} Clausius-Clapeyron equation and integration of the resulting equation provided the vapour pressure data at various temperatures. These values were used in the program VAPFIT to estimate the constants of the vapour pressure equation (see Appendix V.3).

The errors which are involved in calculation of physical properties of formaldehyde does not affect the accuracy of calculations since the significance of the physical properties of formaldehyde in the calculations is reduced by the very low concentration of free formaldehyde in the liquid phase.

Although very large errors up to 20 percent were involved in the calculation of the physical properties, a good accuracy was obtained from the results of the vapour-liquid equilibrium calculations. This may be explained by considering that the involved errors were either offset or absorbed by the values of the estimated binary parameters.

7.8 DISCUSSION OF RESULTS

7.8.1 Estimated Parameters

The parameters were estimated for all the possible binary systems comprising the quinary formaldehyde-hemiformal-methanol-methylene glycol-water system (see Appendix XIV). The binary system for any two condensable components is characterised by the Wilson equation binary parameters. Systems containing formaldehyde, which is treated as a noncondensable component, are characterised by the Wilson single parameter and Henry's constant. However, in the parameter estimation it was found that the program was unable to estimate the Henry's constant due to the reasons mentioned in Section 7.3. Therefore the Henry's constant was estimated, assuming ideal vapour and liquid phases (see Appendix XIV). Although this assumption may prove wrong for the formaldehyde system, it would provide some rough estimate of the Henry's constant values. Nevertheless the estimated Henry's constants have no significant effect on the phase equilibria calculations. This can be explained by considering the Wilson single energy parameter for formaldehyde in water which was the reference component. This value of Wilson's parameter was found to have an unusually large positive value (465.672 kJ/mol). The activity coefficient of the free formaldehyde was reduced to almost zero by the effect of a large positive Wilson energy parameter. The Wilson parameter for binary systems involving formaldehyde

with other components was also found to be equal to zero because these parameters were calculated from the parameters for formaldehyde in the reference solvent. It can be concluded from the low activity coefficient and small concentration of formaldehyde in the liquid phase that the bulk of the free formaldehyde in the vapour phase has been produced by the decomposition of methylene glycol and hemiformal to formaldehyde, methanol and water. Therefore the values of Henry's constant become redundant if the free formaldehyde in the vapour phase is produced from the decomposition of other components rather than direct evaporation of free formaldehyde from the liquid phase.

The unusual large positive or negative values for Wilson's energy parameters (maximum of 4181.814 kJ/mol) are thought to be caused by the vapour phase reaction where the components are produced by the association or dissociation, thus reducing or increasing the amount of the component entering the vapour phase by evaporation.

The calculations for the parameter estimation were based on the isobaric data at the pressure of the experiments. The isobaric data were used because no reliable data was available at other pressures. However, the use of isobaric data could be partly justified by the physical behaviour of the system. The boiling temperature range of formaldehyde-methylene glycol-water system was just less than 3°C for the whole formaldehyde content

range and the boiling temperature range of the quinary system was just less than 30°C over the entire concentration range. Therefore the binary energy parameters could be estimated and averaged over the temperature range. Furthermore the Wilson energy parameters were assumed to be independent of the temperature.

The parameters were estimated by minimising the difference between the calculated and experimental pressure values. The vapour phase mole fractions were not used in the calculations to estimate the parameters thus reducing the problem to estimating the vapour phase mole fraction and temperature.

The root mean square deviation of the calculated pressure was found to be 0.00246 atmospheres. (0.2493 kNm^{-2}) for the quinary system. Considering the complexity of the system, it was concluded that a representative model of the phase equilibria of the system had been achieved.

7.8.2 Vapour-Liquid Equilibrium

The vapour-liquid equilibrium calculations were performed in program BUBLDILF for the ternary and quinary systems. The results for these calculations were tabulated in appendix XII for both systems. The entire experimental concentration range which was encountered in the distillation of formaldehyde at atmospheric pressure was covered by the data. The calculated and

experimental values of the vapour phase mole fractions are represented in graphical form for comparison (see figures 7.1 to 7.5).

Several methods have been derived and reported in the literature for thermodynamic consistency tests of experimental data. These methods have been critically reviewed by Gibson-Robinson (170). However, it was concluded that the existing consistency tests could not be fully applied to these systems for the following reasons.

The consistency tests are applicable to binary data. Since many of the binary systems comprising the quinary system are hypothetical, the binary consistency tests cannot be applied.

An investigation over the full concentration range cannot be carried out due to the effect of the chemical reaction on the concentration of the components, particularly as the free formaldehyde concentration is reduced by the chemical reaction to less than 0.1 mole percent even at high formaldehyde contents.

Large deviations which are not due to the inconsistency of the data or the method could have been caused by the lack of accurate physical property data and insufficient information about the reaction mechanism. Also consistency tests could not be applied over the concentration range of 0.01 to 0.12 mole fraction of methanol, where a correction for the vapour phase mole fraction had to be introduced.

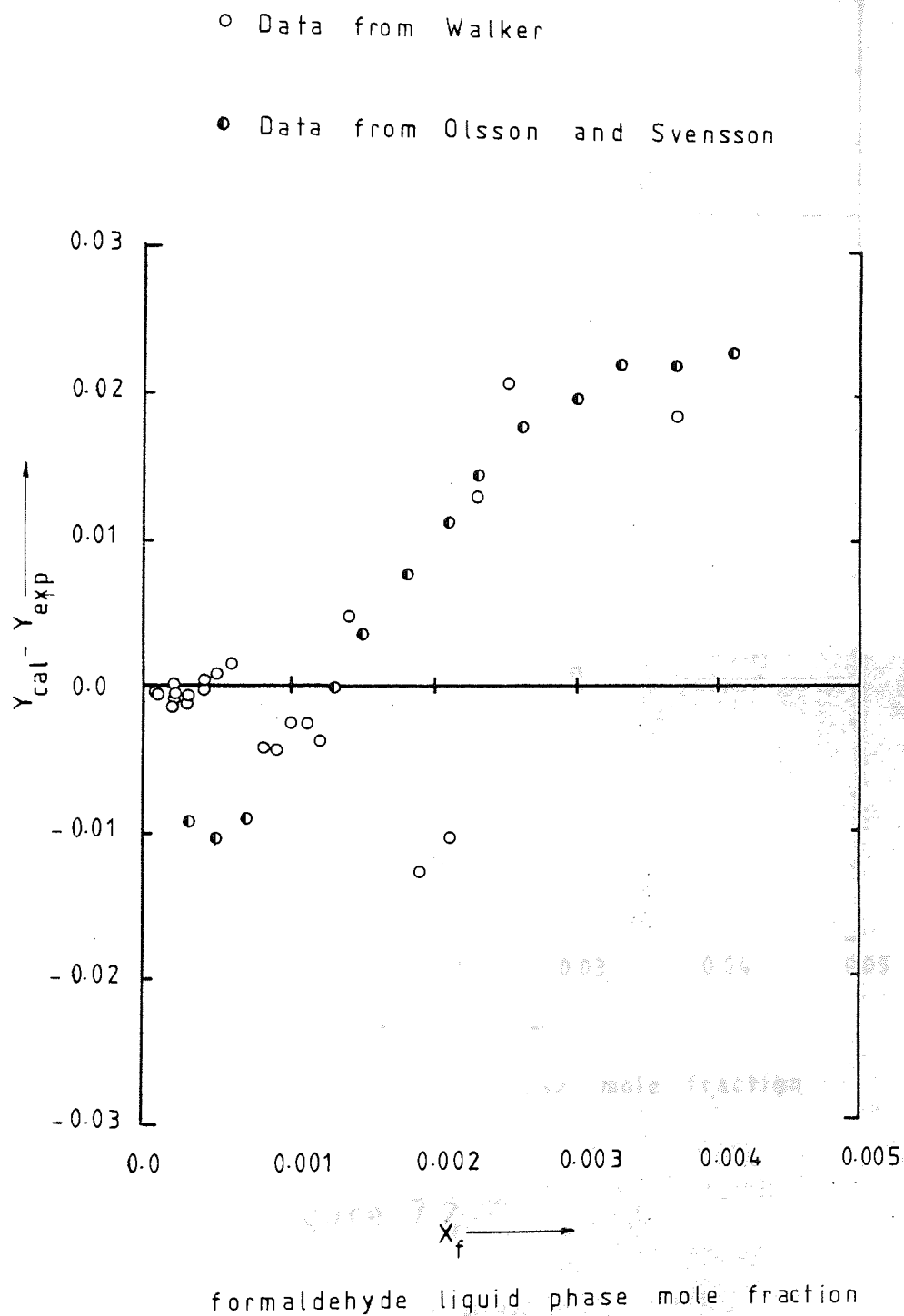


Figure 7.1

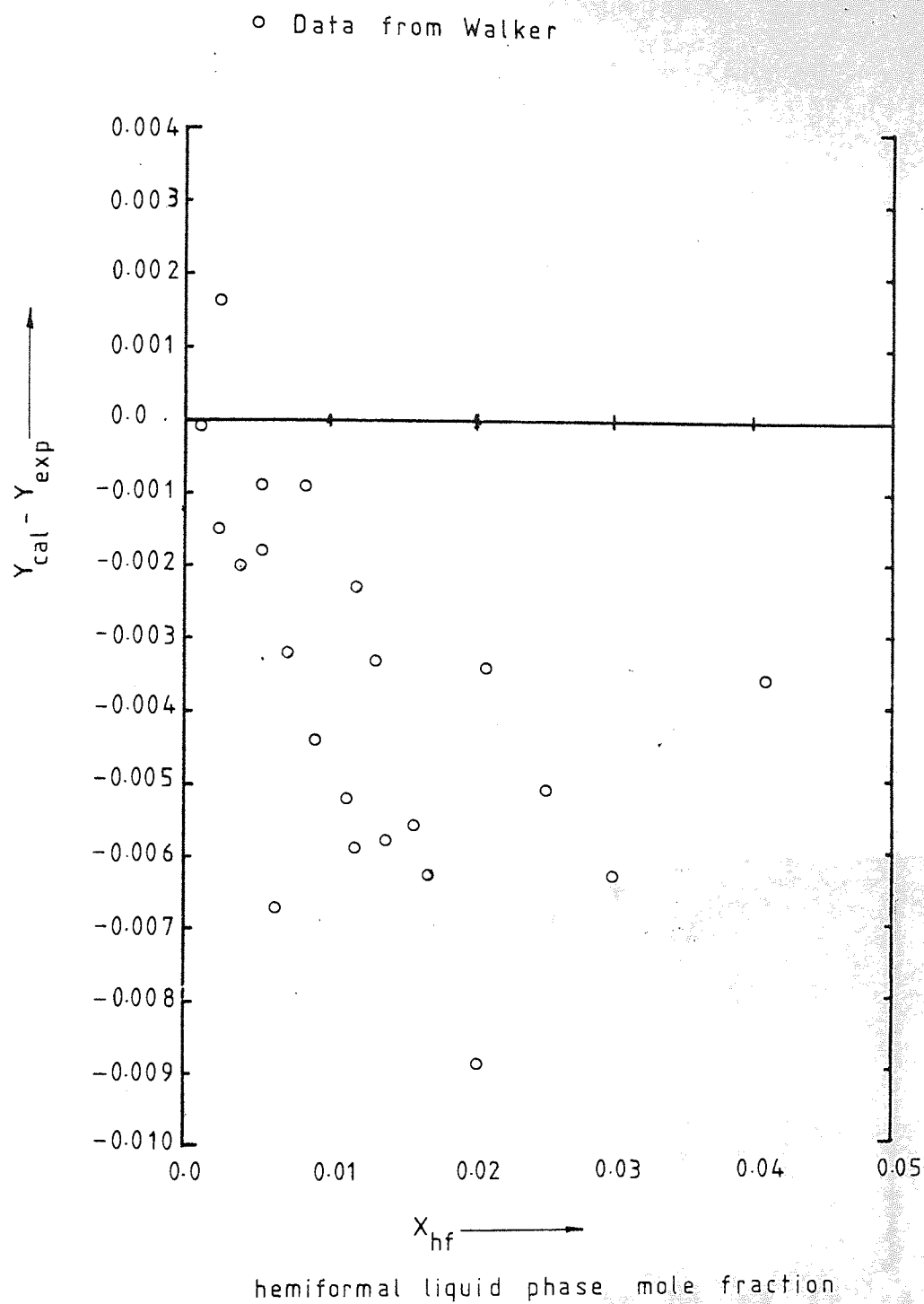


Figure 7.2

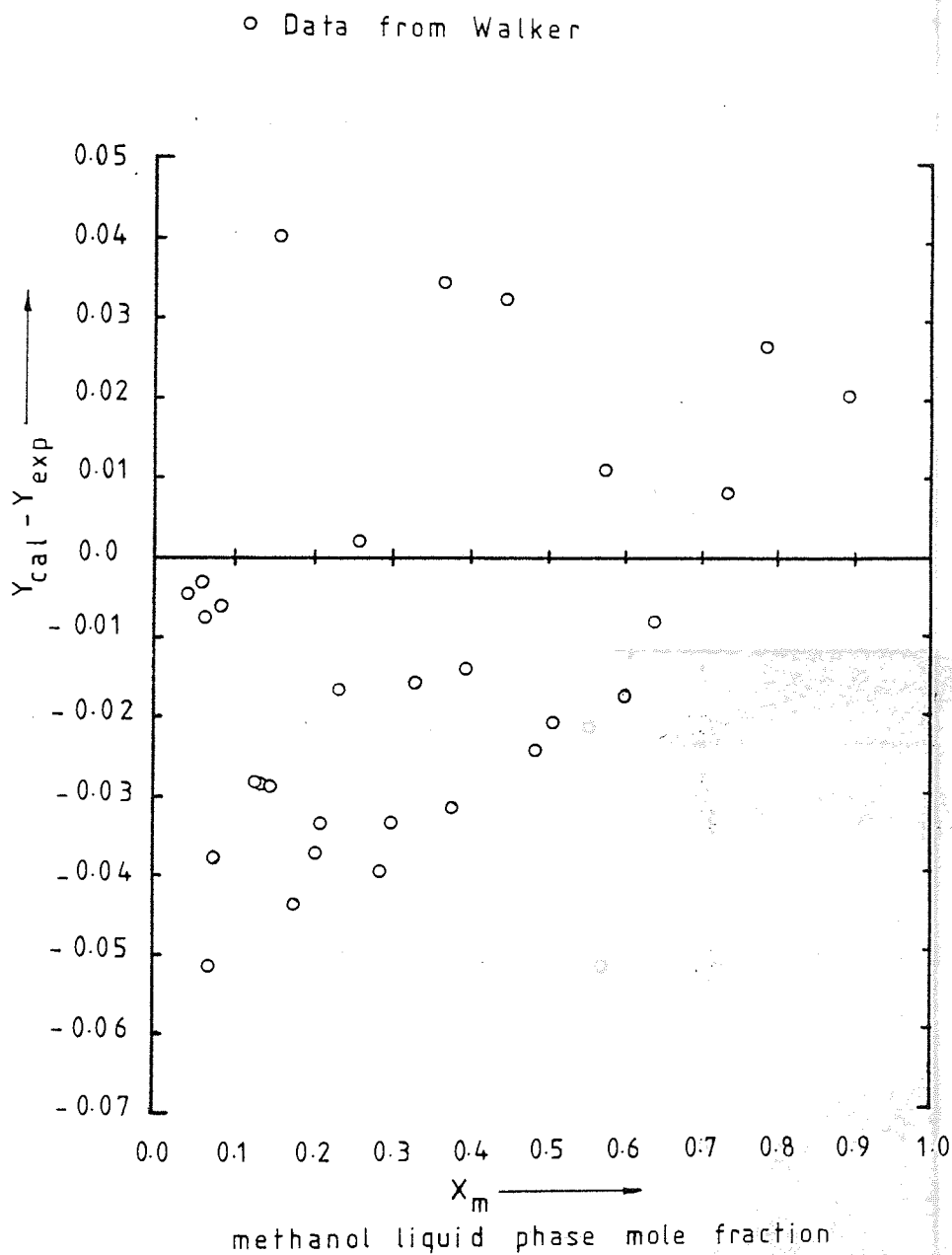


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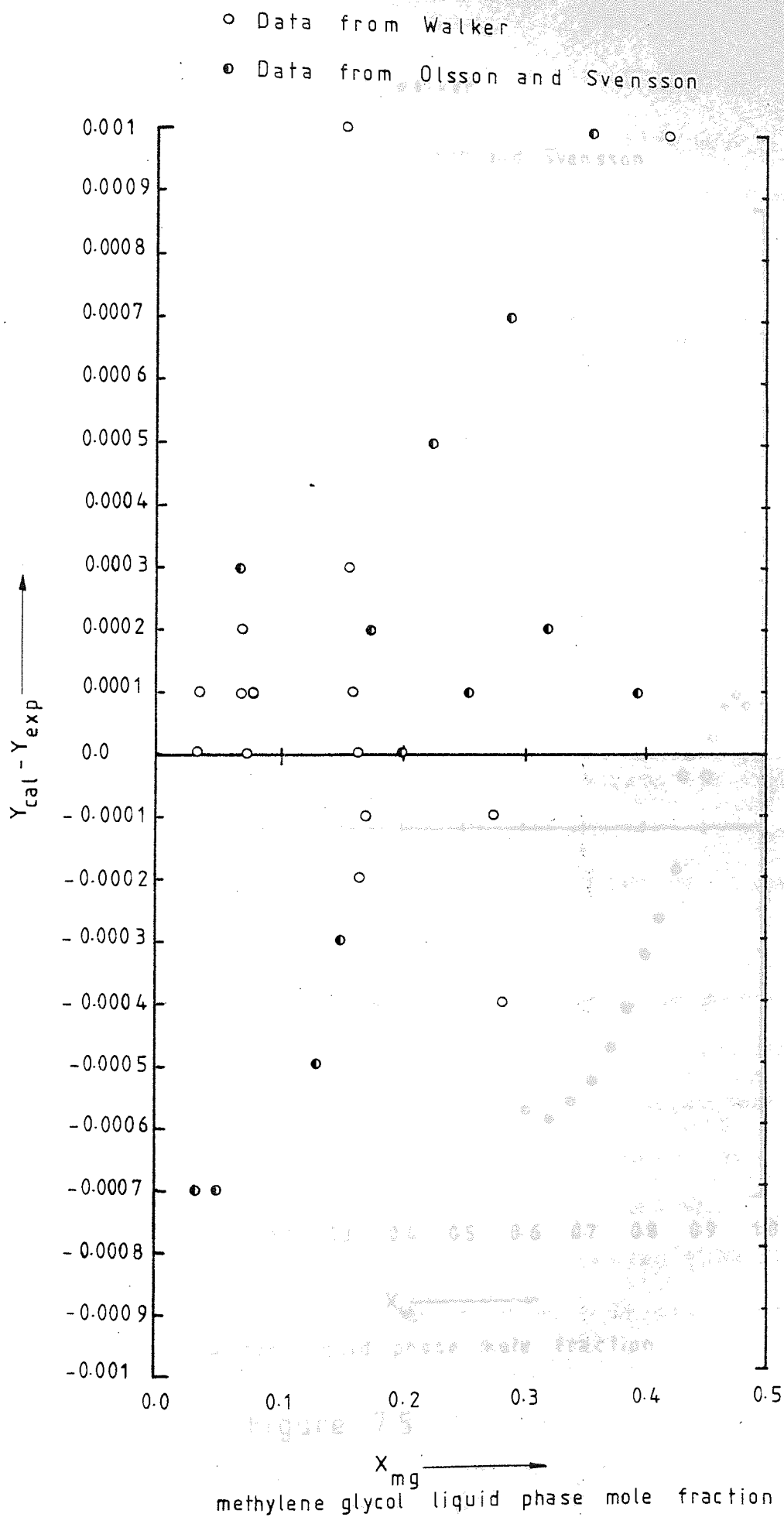


Figure 7.4

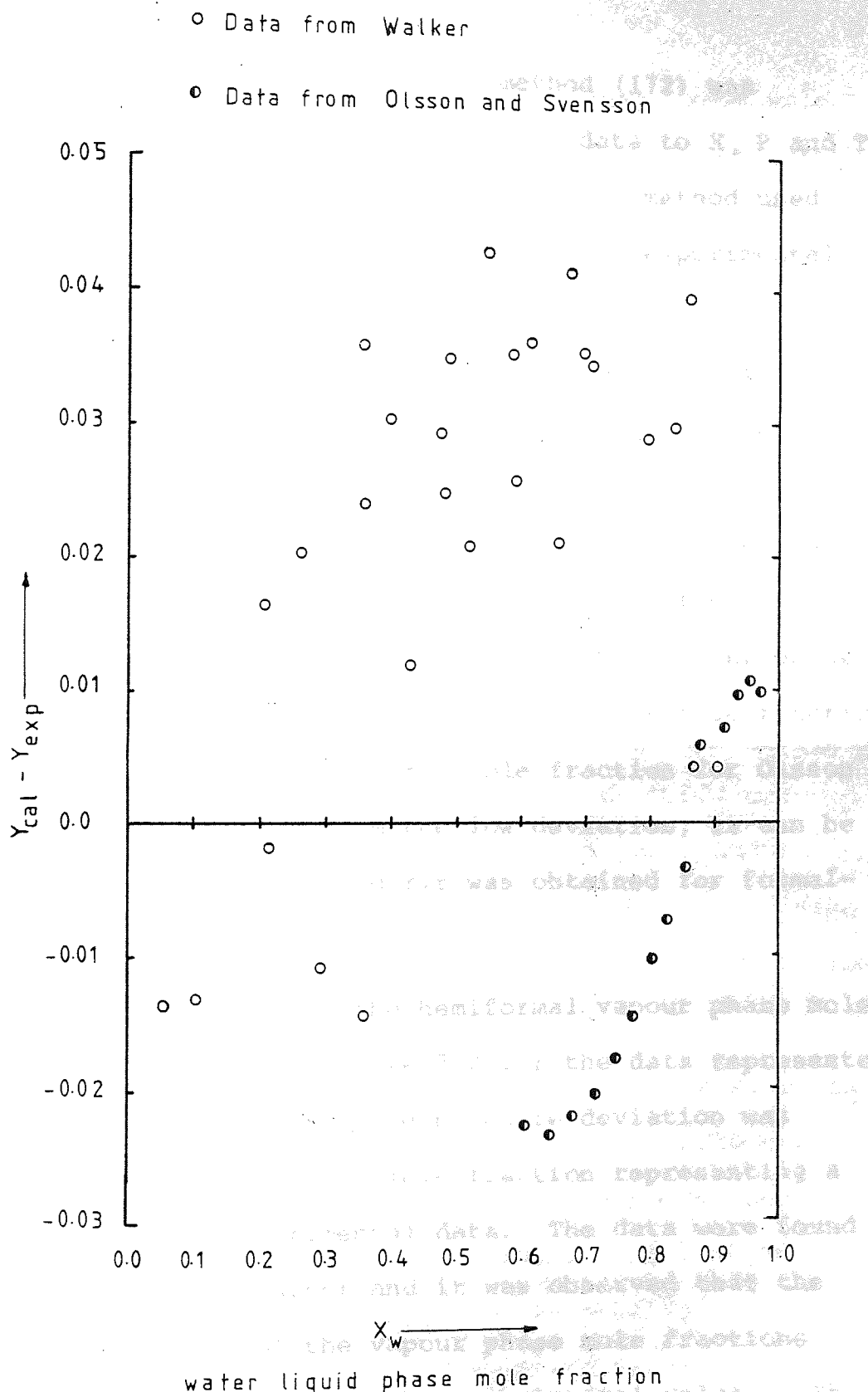


Figure 7.5

However, since the Barker method (172) was employed in reducing the X,Y, P and T data to X, P and T data, the consistency of the data and the method used should be reflected in the calculated and experimental vapour phase mole fractions.

A random scatter is obtained in Figure 7.1 for free formaldehyde for the data represented by Walker (41). A systematic deviation following an S shape pattern is obtained for the data reported by Olsson and Svensson (73), which is also plotted in Figure 7.1. The root mean square deviation for the formaldehyde vapour phase mole fraction was calculated to be 0.002734 mole fraction for Walker's data and 0.003869 mole fraction for Olsson and Svensson's data. From the low deviation, it can be concluded that a very good fit was obtained for formaldehyde.

The deviation of the hemiformal vapour phase mole fractions is shown in Figure 7.2 for the data represented by Walker (41). The root mean square deviation was calculated to be 0.001795 mole fraction representing a good fit to the experimental data. The data were found to have a random scatter and it was observed that the calculated values of the vapour phase mole fractions were generally lower than the experimental values. This difference was probably caused by the lack of accurate physical property data, particularly the vapour pressure data for hemiformal.

The deviation of the methanol vapour phase mole fractions is shown in Figure 7.3 for the data represented by Walker (41). The root mean square deviation was calculated to be 0.005590 mole fraction. A random scatter was obtained with larger deviations for methanol.

A very good fit was obtained for methylene glycol with a root mean square deviation of 0.00323 mole fraction for Walker's data and 0.000134 mole fractions for Olsson and Svensson's data. From Figure 7.4 Walker's data were randomly scattered whilst systematic deviations were shown in Olsson and Svensson's data.

Similar deviations for water were plotted in Figure 7.5 and a root mean square deviation of 0.005084 mole fractions was obtained for Walker's data and 0.003965 mole fractions for Olsson and Svensson's data. The same systematic deviation was observed for Olsson and Svensson's data.

The uncertainty in Olsson and Svensson's data was shown by the systematic deviation to be far below that of Walker's data and therefore it was concluded that Olsson and Svensson's data was a better source. The lack of accurate physical property data, especially for the chemical reaction constants and vapour pressure of some of the components, are thought to be responsible for the magnitude of the deviations.

7.8.3 Distillation Results

The results from distillation experiments are

tabulated in Appendix XII. The conditions for the experiments can be found in Appendix XII.3 and the results from the experiments and the mathematical model are tabulated in Appendix XII.4. The actual efficiency values for each of the components in each tray are tabulated in Appendix XII.5 for all the experiments.

In the experimental distillation results it was observed that the decrease in the formaldehyde concentration was much larger on plates above the feed plate. This phenomena was thought to be due to the hot feed evaporating the more volatile components namely free formaldehyde, hemiformal and methanol. Since the concentration of free formaldehyde is very low in the liquid phase, the increase in the formaldehyde content of the vapour phase would be negligible compared with the hemiformal and methanol concentration.

It was observed that the separation was reduced when the feed rate was increased. This effect can be explained by the shorter contact time between the vapour and the liquid phase on the plate below the feed plate.

When the heat input was increased, a better separation was obtained. The system was observed to foam and at larger heat input severe foaming developed causing increased contact between the vapour and liquid phases resulting in a better separation. Furthermore, the escape of free formaldehyde from the top of the column was found to increase at higher boil-up rates, resulting in an

enriched reflux.

For methanol concentrations between 2 and 8 weight percent in the feed, the feed plate position was found to be more suitable in the top section of the column. The amount of methanol in the bottom product is reduced by the action of a larger number of plates below the feed plate. Consequently a larger concentration of methanol would be obtained in the top product. Similarly, it was found that, for feed streams containing less than 2 weight percent methanol, the lower plates would be more suitable as a feed plate where the action of the larger number of plates above the feed plate could be used to obtain a better separation. Thus the amount of methanol is minimised in the bottom product.

The separation was increased by larger plate hold-ups which created a longer contact time between the vapour and liquid phases.

At higher reflux ratios a better separation was obtained and this was thought to be caused by higher rectification of the vapour phase.

The performance of the mathematical model can be assessed by the comparison of the experimental and calculated data for the distillation of formaldehyde. Good agreement was obtained between the experimental and calculated results despite the complexity and lack of data for the system (see Figures 7.6 to 7.10 for some arbitrary

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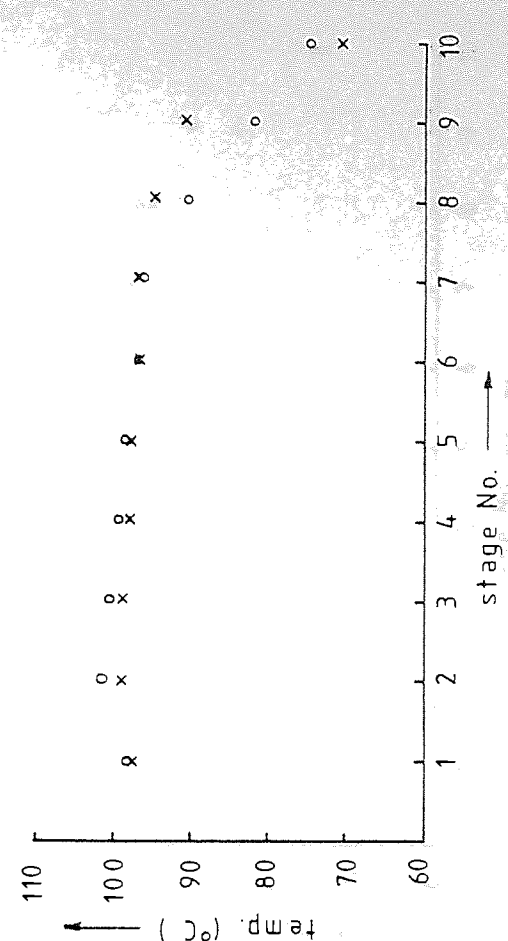
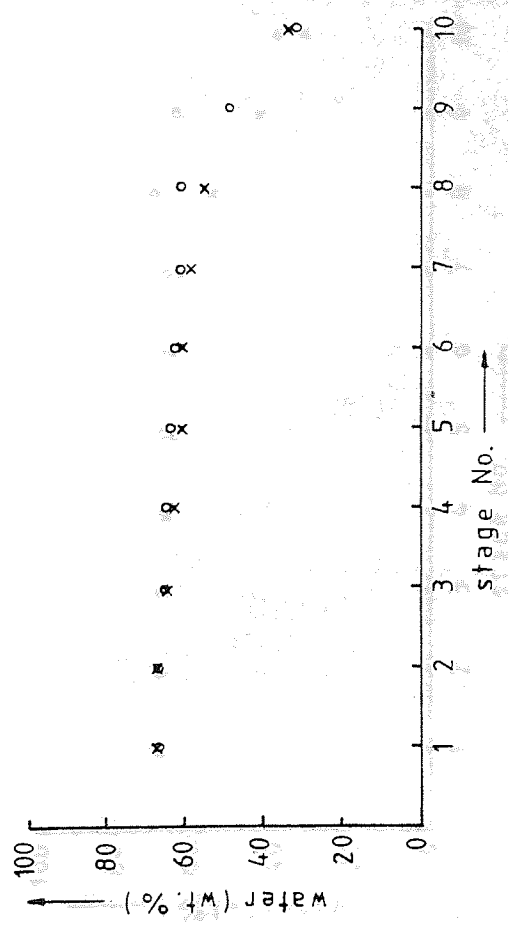
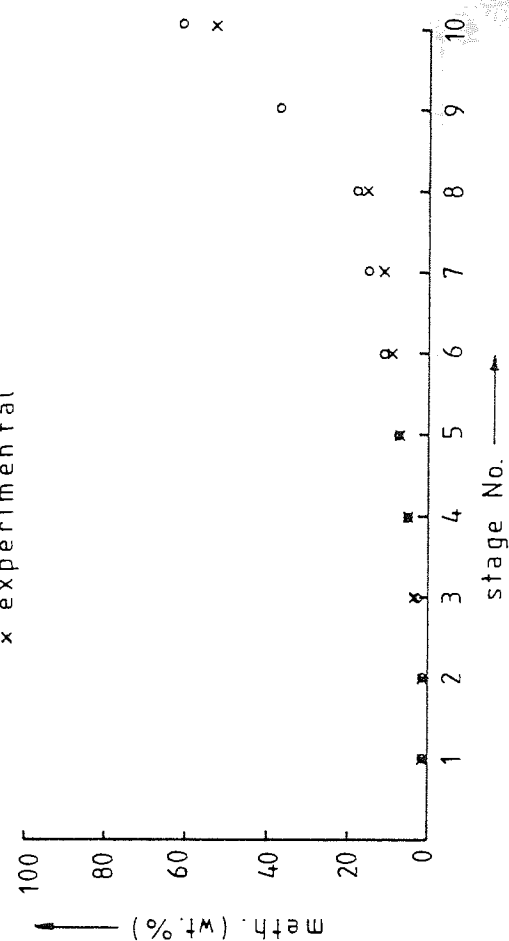
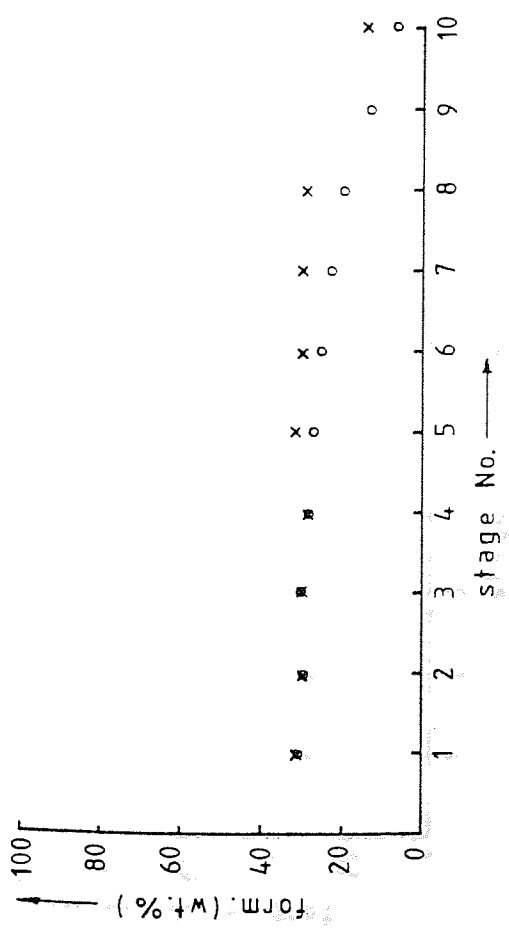


Figure 7.6 experiment No. 5

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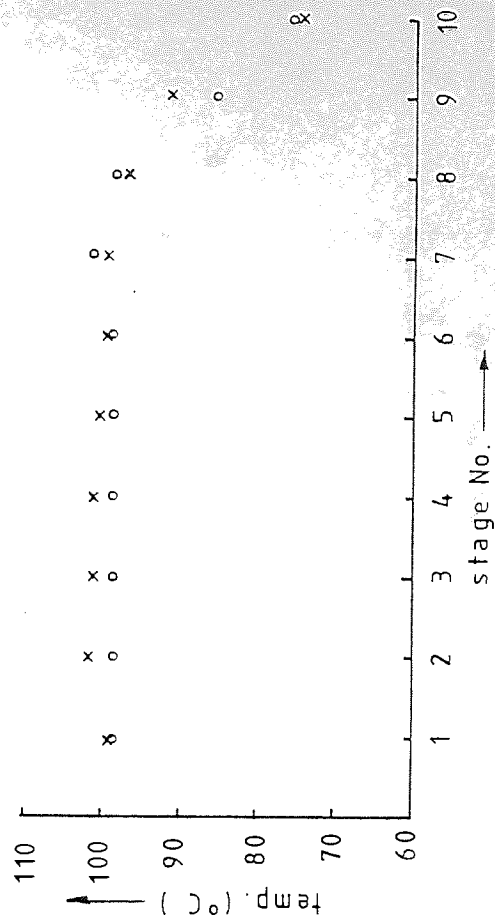
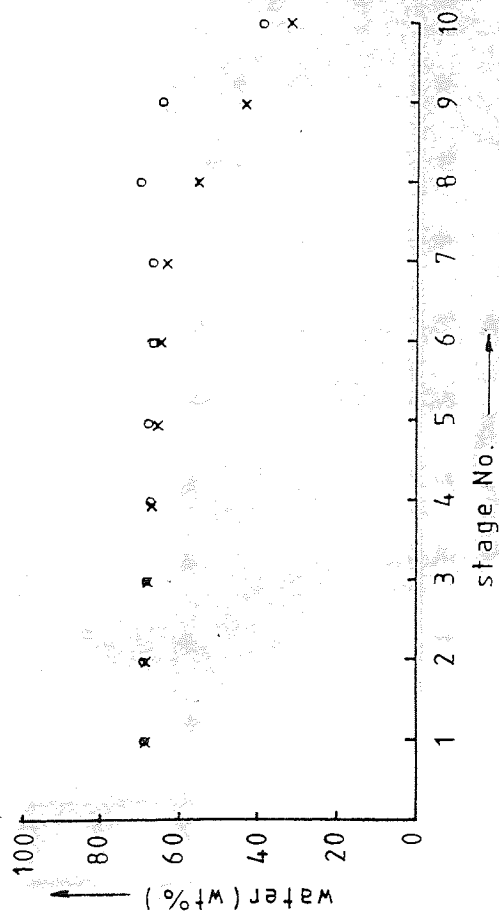
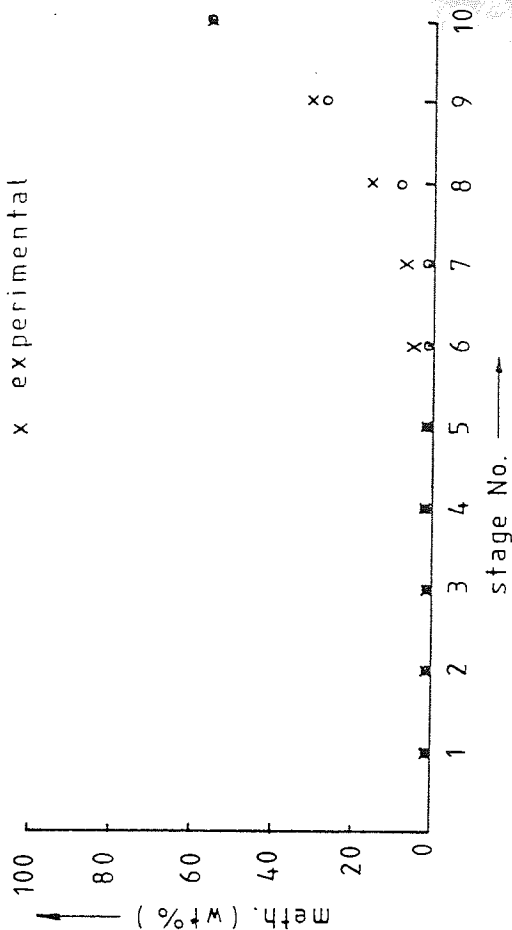
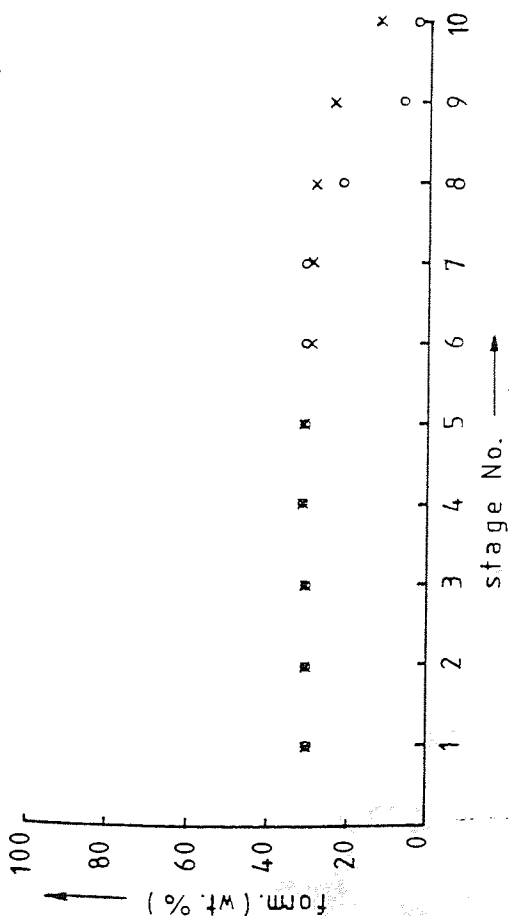


Figure 7.7 experiment No. 11

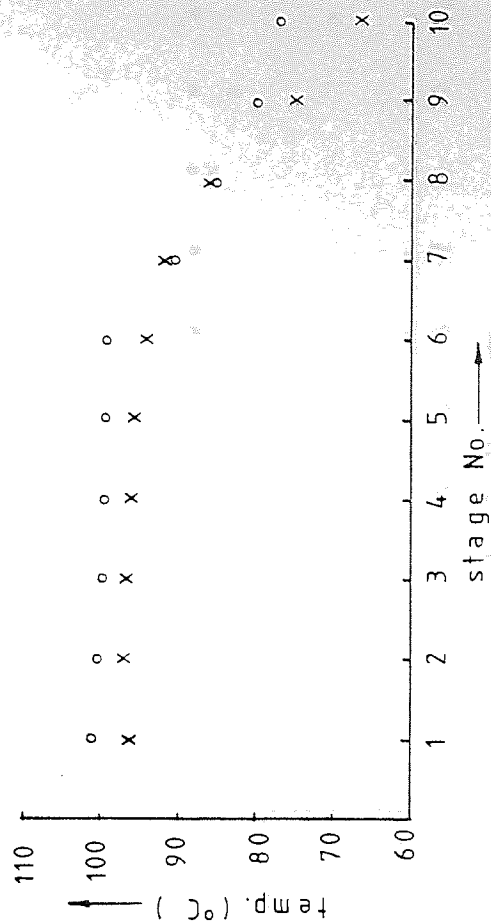
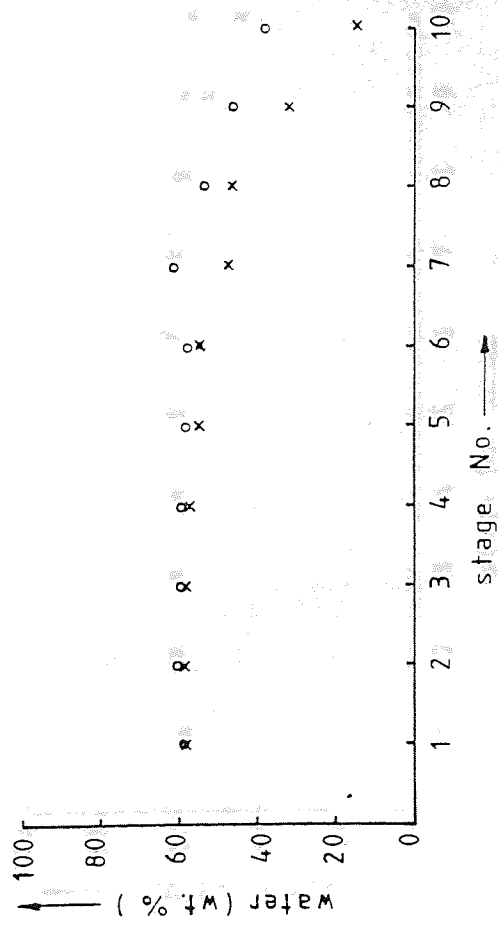
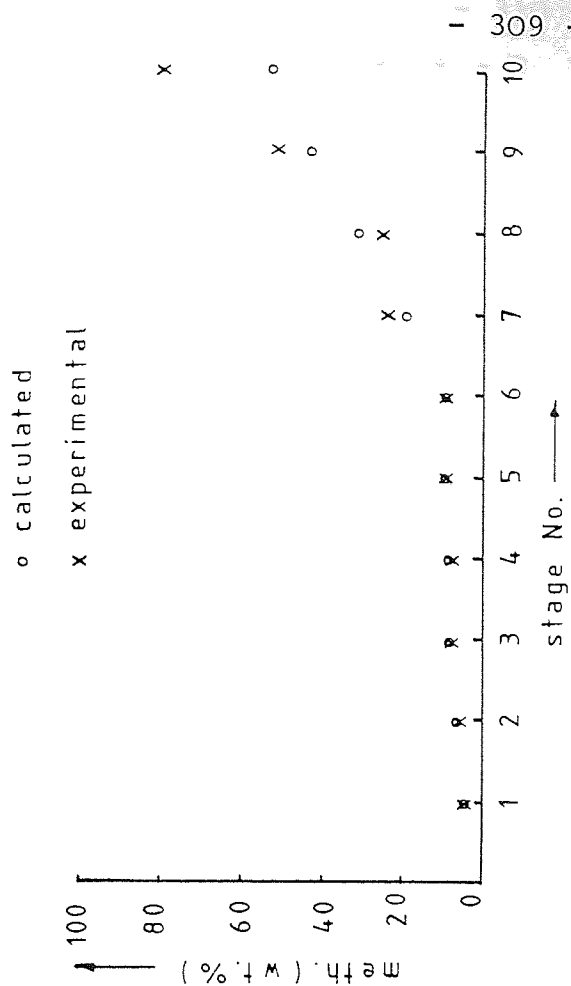
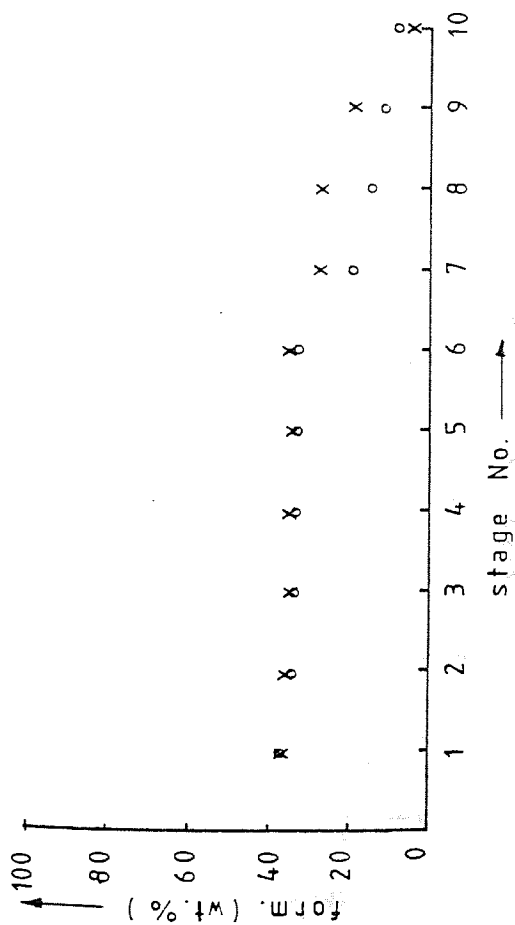


Figure 7.8 experiment 16

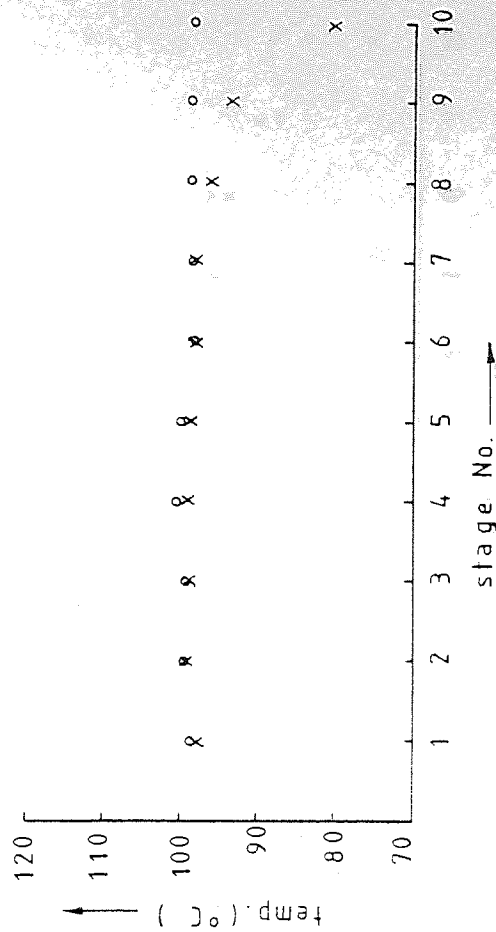
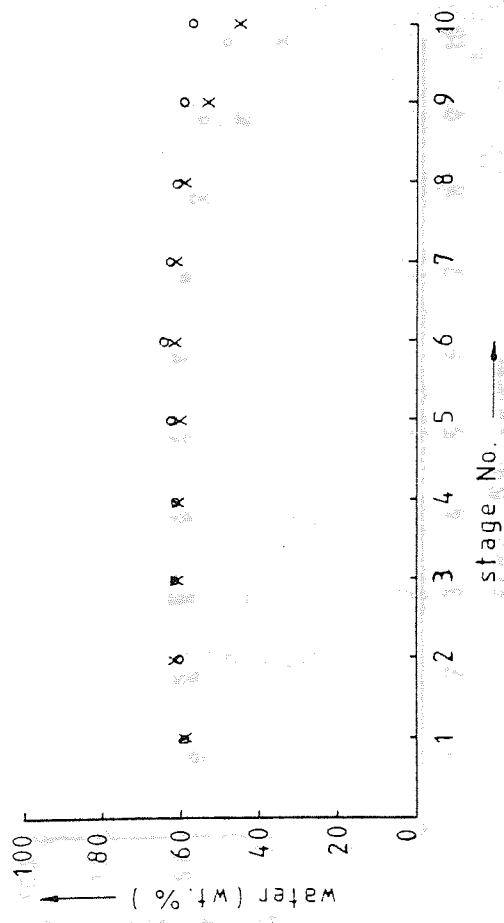
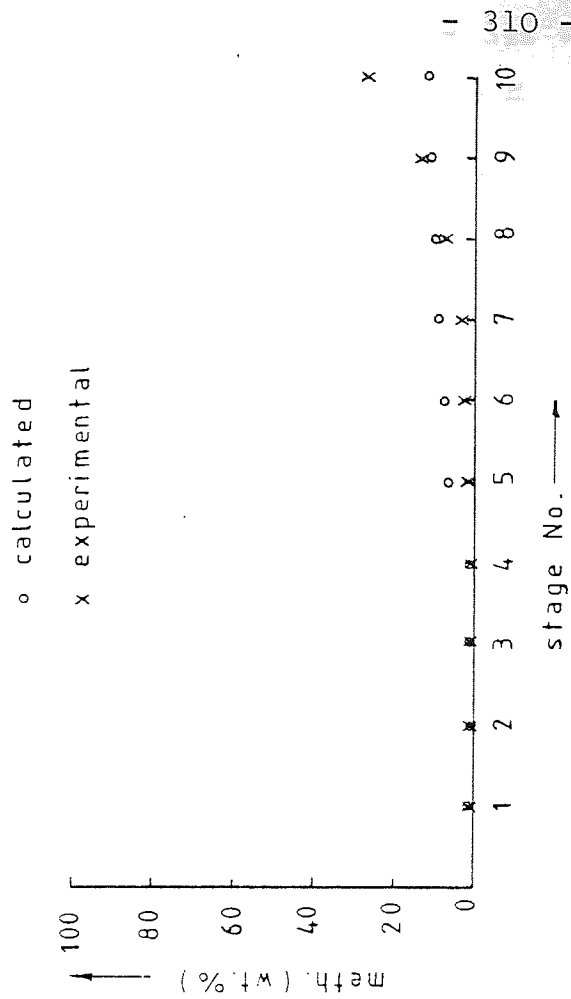
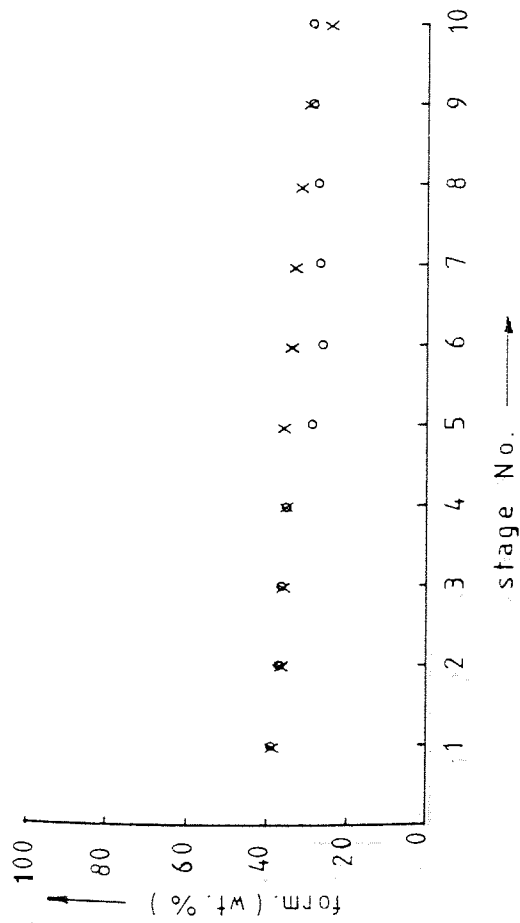


Figure 7.9 experiment 20

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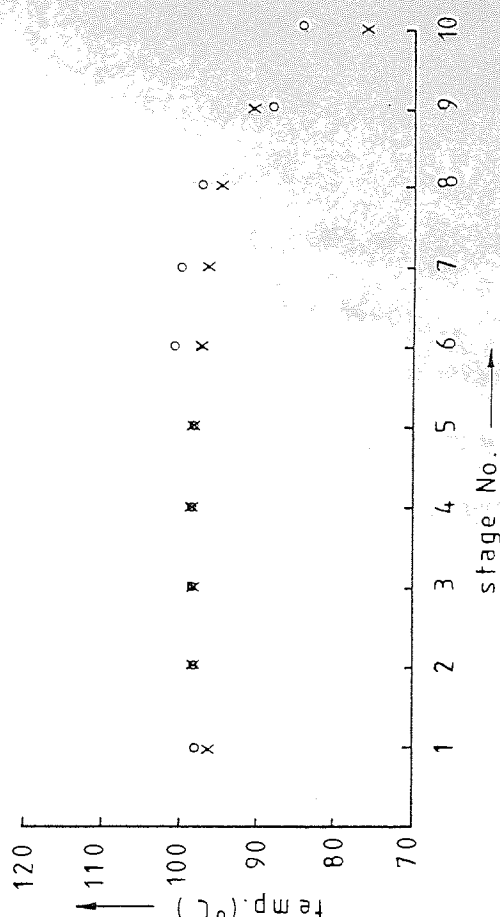
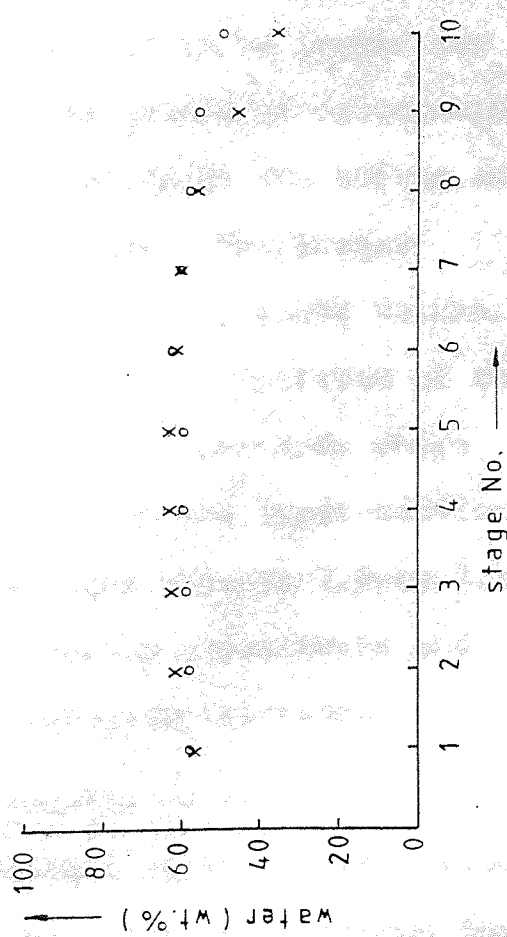
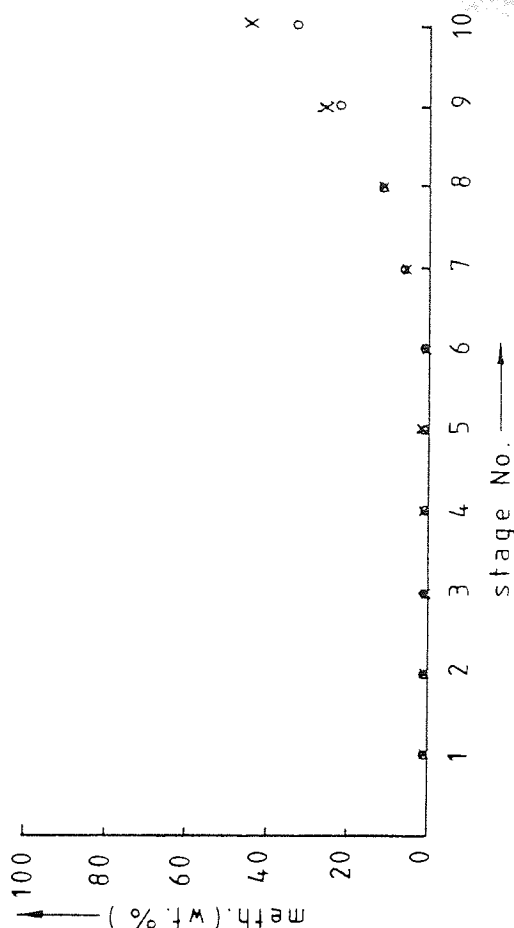
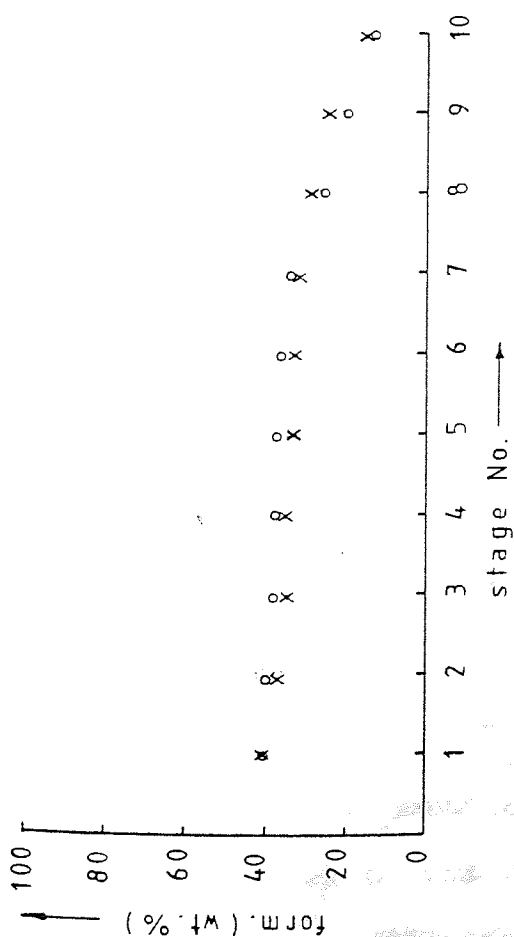


Figure 7.10 experiment 25

experiments).

The main cause of the deviation is attributed to the insufficient plate efficiency estimation technique. Although the values of the calculated plate efficiencies were corrected for each component, further refinements are still required. The best method of developing plate efficiency estimation technique would be to use accurate measurement of vapour phase concentrations on each plate.

The difference between the calculated and experimental results are presented in the form of a root mean square deviation for each plate. The mean square deviations are listed in Table 7.2 for each plate for all the experiments.

The deviations would be expected to be larger for the top plates as the tray to tray method of calculation was used for the modelling, commencing at the bottom and iterating up to the top of the column. The errors therefore would be accumulated in the top plate values. This conclusion can be observed from a comparison of the deviations for the plates in the lower sections where smaller deviations were obtained with the upper section where larger deviations occurred (see Figures 7.6 to 7.10). The average deviations for the entire experiments and components was found to be 0.0129 weight fractions.

The deviations could reasonably be reduced by a minor modification to the condenser in the distillation column, by using an efficient and accurate technique for

analysing the vapour samples and by developing a suitable plate efficiency estimation technique.

From an overall review of the calculations and the incorporated error, the errors in the vapour-liquid equilibrium calculations were found to be much less than the uncertainties in the experiments and the distillation calculations. A rigorous description of the system is represented by the tray to tray calculations in the distillation column and therefore the deviations between the experimental and calculated distillation results are caused mainly by the errors involved in the tray efficiency estimation. However the lack of accurate physical property data also has caused a major effect on the deviations.

TABLE 7.2 THE DEVIATIONS OF CALCULATED AND EXPERIMENTAL LIQUID PHASE WT. FRACTION IN DISTILLATION.

Stage No.	ΔX_1 Average formaldehyde wt. fraction	ΔX_2 Average methanol wt. fraction	ΔX_3 Average water wt. fraction	ΔX Average plate wt. fraction
1	0.0004	0.0011	0.0008	0.0008
2	0.0030	0.0028	0.0039	0.0032
3	0.0079	0.0059	0.0051	0.0063
4	0.0161	0.0104	0.0055	0.0107
5	0.0135	0.0154	0.0081	0.0123
6	0.0123	0.0151	0.0092	0.0122
7	0.0122	0.0116	0.0132	0.0123
8	0.0135	0.0164	0.0169	0.0156
9	0.0243	0.0323	0.0327	0.0298
10	0.0158	0.0357	0.0261	0.0259

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CHAPTER 8

FUTURE WORK

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8. FUTURE WORK

The investigations carried out in this work have provided a basis for future work on the mathematical modelling of the distillation of formaldehyde. The accuracy and reliability of the mathematical model could further be improved by refinements to the calculation techniques and the experimental methods.

Thus future work could be carried out in five main areas.

8.1 VAPOUR-LIQUID EQUILIBRIUM

The performance and accuracy of the prediction of the vapour-liquid equilibrium data has been dependent on the quality of the available experimental data. A very good model can not be expected to perform well with poor data. As has been mentioned in previous chapters, the available experimental vapour-liquid equilibrium data were either not available or of poor quality. Therefore, one major area of future work would be the determination of accurate experimental data.

The vapour-liquid equilibrium model in this work was developed in a general form and can be applied to other reacting systems with minor modifications. Therefore, the performance of the model could be checked by using data from other well documented and understood systems. Changes in the expressions for the reaction constants

and the routines for the calculation of the chemical equilibrium conditions would be the only minor modification required for the program.

Various other liquid or vapour models have been proposed in the literature, (see Chapter 3), and these models could be usefully applied to the formaldehyde system. Several semi-empirical relationships were incorporated with the vapour-liquid model. The effect of alternative empirical relationships could be assessed for the formaldehyde system by modifying the existing model with alternative relationships.

The principle of the model developed in this work can be used to develop a program for the reduction of any of the four characteristic variables X , Y , P and T . The various types of the model can be used in different calculation procedures in the distillation calculations.

Existing consistency tests must be modified to incorporate the effect of a chemical reaction and to allow for multicomponent systems which can not be analysed into the constituent binary systems. Only then can an accurate measure of the vapour-liquid equilibrium calculation performance be obtained.

8.2 DISTILLATION CALCULATIONS

The distillation calculations using the simultaneous solution methods which resulted in divergent and unstable

equations could be tried with a different type of phase equilibria calculation, such as the reduction of any of X, P or T instead of Y as tried in this work. If X was reduced, then the top of the column would provide a starting point for the calculations.

A better representation of the system and a simpler definition of plate efficiency was given by the first model which was based on the liquid and vapour phase reactors. In this model, the plate efficiency could distinctively be defined in terms of the efficiency of the two reactors for the chemical reaction and the conventional tray efficiency for the phase equilibrium. Convergent results may be given by this model if more accurate and representative definitions of chemical reaction constants are available. Better and more accurate vapour-liquid equilibrium calculations would be obtained if activity coefficient dependent chemical equilibrium constants are available.

The mathematical model in this work was only tried at atmospheric pressure. Provided that the experimental data are available the capability of the model can be tested to handle a wider range of pressures. Similarly the model could be applied and checked against information from industrial distillation columns.

8.3 EFFICIENCY CALCULATIONS

The significant deviations in the distillation calculations were caused by inadequate estimation of the plate efficiency. The A.I.Ch.E. method (133) was found to give an averaged value over the whole column whereas more accurate data were needed for each plate. The results of the distillation calculations were generally improved by the correction of the efficiency data but a more appropriate method is needed for plate efficiency estimation.

Two different methods could be applied for developing an accurate and appropriate method for the plate efficiency estimation technique.

The first method could be based on the separation of the chemical reaction efficiency from that of the distillation plate. This could be performed by employing the first proposed model for the distillation plate with chemical reactors in both the vapour and liquid phases, provided that convergence is obtained with this method. The method for multicomponent plate efficiency estimation can be applied together with the chemical reactors efficiency.

The second method could be based on the actual measurement of the plate efficiency. This can be done by accurate vapour sampling. A model could be fitted

to the experimental data in the form of equations used in the A.I.Ch.E. plate efficiency estimation method. The constants of the equation could be calculated using a regression algorithm technique, similar to the method used by Olsson and Svensson (73) for the formaldehyde-water system.

The same procedure could be repeated for the Murphree efficiencies based on the liquid concentration and a polynomial could be fitted to the experimental data obtained in this work.

8.4 PHYSICAL PROPERTY DATA

The accuracy of all the calculated parameters was dependent on the quality of the physical data used in the calculations. The experimental methods of measuring the physical properties cannot be utilised because two of the components, hemiformal and methylene glycol, cannot be separated in the pure form. Therefore more accurate methods are needed to estimate these values.

The vapour pressure data on which the vapour-liquid equilibrium calculations are based, must be measured or estimated more accurately. The chemical reaction equilibrium constants must be defined more accurately as a function of temperature.

8.5 DISTILLATION COLUMN

Flexibility in terms of the construction and the number

of controllable parameters, was provided in the design of the distillation column. However, the flexibility could be increased further by some modifications.

The method of vapour sampling was found to be inaccurate due to the high volatility of free formaldehyde in the vapour phase: the total condensation of the vapour phase could not be achieved using an ordinary condensation chamber. More accurate vapour phase sampling might be obtained by an on-line gas analyser such as a mass spectrometer. A hypodermic needle could be placed in the vapour sampling arm and the needle could be extended to the outside of the cabinet, where the probe of the mass spectrometer could be connected. No condensation would occur in the connection lines due to the high vacuum in the mass spectrometer. Thus a quick and accurate measurement of the vapour sample could be achieved without polymerisation of the sample or escape of free formaldehyde.

The escape of free formaldehyde from the top of the condenser has contributed to the deviation between the calculated and experimental results for the distillation column. This problem could be overcome by a slight modification of the condenser. If the vapour entering the condenser were to be bubbled through the cold liquid leaving the condenser, then the free formaldehyde in the vapour phase would be scrubbed into the liquid phase and thus the loss of formaldehyde would be reduced.

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PHASE REACTIONS

with methanol and water
the glycol are

(1.1)

(1.2)

APPENDICES

Chemical reaction

XO3, XO4 and XO5 for the

glycol and water

components after the equilibrium

X1 to X5 for the same

the number of moles of

first and second reaction,

produced in the two reactions

of the original mixture, $ol+fl$

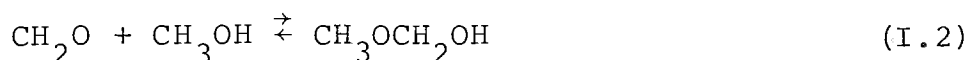
assumed.

of moles after equilibrium = $l-ol-fl$

(1.3)

APPENDIX I.1 LIQUID PHASE REACTIONS

The reactions of formaldehyde with methanol and water producing hemiformal and methylene glycol are represented by equations I.1 and I.2.



The equations of the liquid phase reaction for the components could be derived from the original mole fractions of each of the components before the reaction. The mole fractions of the components before the chemical reaction are denoted by X01, X02, X03, X04 and X05 for formaldehyde, hemiformal, methanol, methylene glycol and water respectively. The mole fractions of the components after the equilibrium has been achieved, are denoted by X1 to X5 for the same components. If α_L and β_L are the number of moles of formaldehyde consumed in the first and second reaction, the amount of moles used or produced in the two reactions are shown in Table I.1.

Thus from one mole of the original mixture, $\alpha_L + \beta_L$ number of moles are consumed.

the total number of moles after equilibrium = $1 - \alpha_L - \beta_L$

$$\text{partial equilibrium relations} \quad (\text{I.3})$$

Table I.1

Component	Number of moles used	Number of moles produced
Formaldehyde	$\alpha L + \beta L$	-
Hemiformal	-	βL
Methanol	βL	-
Methylene glycol	-	αL
Water	αL	-
Net Balance	$2(\alpha L + \beta L)$	$\alpha L + \beta L$

The mole fractions before and after equilibrium are shown in Table I.2.

Table I.2

Component	Mole fraction before reaction	Mole fraction at equilibrium
Formaldehyde	X_{01}	$X_1 = \frac{X_{01} - \alpha L - \beta L}{1 - \alpha L - \beta L}$
Hemiformal	X_{02}	$X_2 = \frac{X_{02} + \beta L}{1 - \alpha L - \beta L}$
Methanol	X_{03}	$X_3 = \frac{X_{03} - \beta L}{1 - \alpha L - \beta L}$
Methylene glycol	X_{04}	$X_4 = \frac{X_{04} + \alpha L}{1 - \alpha L - \beta L}$
Water	$\frac{X_{05}}{\Sigma = 1.0}$	$X_5 = \frac{X_{05} - \alpha L}{1 - \alpha L - \beta L}$

Values of X_1 to X_5 are substituted into equations I.4 and I.5 which represent the chemical equilibrium relationships (41,43). The numerical values of K values and their

dependence on temperature are given in Appendix III.

$$K_1^L = \frac{X_1}{X_4} \quad (\text{as defined by Drumm and Le Blanc(43)}) \quad (\text{I.4})$$

$$K_2^L = \frac{X_2}{X_1 \cdot X_3} \quad (\text{I.5})$$

Equation I.4 is solved for the variable α_L resulting in equation I.6.

$$\alpha_L = \frac{X_{O1} - \beta_L - K_1^L X_{O4}}{K_1^L + 1} \quad (\text{I.6})$$

Substitution of α_L from I.6 into equation I.5 results in the definition of β_L as a function of known variables.

$$\begin{aligned} & \beta_L^2 (-K_1^L - K_1^L K_2^L) + \beta_L (-K_1^L \cdot X_{O2} + K_1^L + 1 - X_{O1} + K_1^L \cdot X_{O4} + K_1^L K_2^L \cdot X_{O1} + \\ & K_1^L K_2^L \cdot X_{O4} + K_1^L K_2^L \cdot X_{O3}) + K_1^L \cdot X_{O2} + X_{O2} - X_{O2} \cdot X_{O1} + K_1^L \cdot X_{O4} \cdot X_{O2} - \\ & K_1^L K_2^L \cdot X_{O1} \cdot X_{O3} - K_1^L K_2^L \cdot X_{O3} \cdot X_{O4} = 0 \end{aligned} \quad (\text{I.7})$$

The values of β_L could be calculated from equation I.7 and substituted into equation I.6 for calculation of α_L . The values of X_1 to X_5 could be calculated from the relationships given in Table I.2.

APPENDIX I.2 VAPOUR PHASE REACTIONS

The calculation procedure for the vapour phase is similar to that of the liquid phase except for the definition of the equilibrium constants. Y_{O1} to Y_{O5} were

denoted for the mole fractions before the reaction and Y_1 to Y_5 for the mole fractions of the components formaldehyde, hemiformal, methanol, methylene glycol and water after the reaction. The number of moles reacted in the first and second reactions are denoted by αV and βV . The mole fractions before and after the vapour phase reaction are denoted in Table I.3.

Table I.3

Component	Mole fractions before reaction	Mole fractions at equilibrium
Formaldehyde	Y_{01}	$Y_1 = \frac{Y_{01} - \alpha V - \beta V}{1 - \alpha V - \beta V}$
Hemiformal	Y_{02}	$Y_2 = \frac{Y_{02} + \beta V}{1 - \alpha V - \beta V}$
Methanol	Y_{03}	$Y_3 = \frac{Y_{03} - \beta V}{1 - \alpha V - \beta V}$
Methylene glycol	Y_{04}	$Y_4 = \frac{Y_{04} + \alpha V}{1 - \alpha V - \beta V}$
Water	$\frac{Y_{05}}{\sum = 1.0}$	$Y_5 = \frac{Y_{05} - \alpha V}{1 - \alpha V - \beta V}$

The chemical equilibrium constants are represented by equations I.8 and I.9 (53). The numerical values and the dependence of K_1^V and K_2^V are given in Appendix III.

$$K_1^V = \frac{P Y_1 \cdot Y_5}{Y_4} \quad (I.8)$$

$$K_2^V = \frac{P Y_1 \cdot Y_3}{Y_2} \quad (I.9)$$

Substitution of Y1 to Y5 into equations I.8 and I.9 and solving the resulting equations for αV would result in equation I.10.

$$\alpha V = \frac{K_1^V \cdot Y03 \cdot Y04 - K_1^V \cdot Y04 - K_2^V \cdot Y02 \cdot Y05 - K_2^V \beta V \cdot Y05}{K_1^V \beta V - K_2^V \cdot Y02 - K_2^V \beta V - K_1^V \cdot Y03} \quad (I.10)$$

Substitution of equation I.10 into equation I.9 and solving the resulting equation for βV , the equation I.11 is obtained.

$$\begin{aligned} \beta V^3 & (-PK_2^V + PK_1^V - K_2^{V^2} + K_1^V K_2^V) + \beta V^2 (PK_2^V \cdot Y03 - 2PK_1^V \cdot Y03 + PK_2^V \cdot Y01 \\ & - PK_1^V \cdot Y01 - PK_2^V \cdot Y02 - PK_1^V \cdot Y04 - PK_2^V \cdot Y05 - 2K_2^{V^2} \cdot Y02 \\ & + K_1^V K_2^V \cdot Y02 + K_2^{V^2} - K_1^V K_2^V - K_1^V K_2^V \cdot Y03 - K_1^V K_2^V \cdot Y04 - K_2^{V^2} \cdot Y05) \\ & + \beta V (-PK_2^V \cdot Y01 \cdot Y03 + 2PK_1^V \cdot Y01 \cdot Y03 + PK_2^V \cdot Y02 \cdot Y03 + 2PK_1^V \cdot Y03 \cdot Y04 \\ & + PK_2^V \cdot Y03 \cdot Y05 + PK_2^V \cdot Y01 \cdot Y02 - PK_2^V \cdot Y02 \cdot Y05 + 2K_2^{V^2} \cdot Y02 \\ & - K_1^V K_2^V \cdot Y02 - K_2^{V^2} \cdot Y02^2 - K_1^V K_2^V \cdot Y02 \cdot Y03 - K_1^V K_2^V \cdot Y02 \cdot Y04 + PK_1^V \cdot Y03 \\ & - 2K_2^{V^2} \cdot Y02 \cdot Y05 + K_1^V K_2^V \cdot Y03 + K_1^V K_2^V \cdot Y03 \cdot Y04) - PK_2^V \cdot Y01 \cdot Y02 \cdot Y03 \\ & - PK_1^V \cdot Y03^2 \cdot Y04 + PK_2^V \cdot Y02 \cdot Y03 \cdot Y05 + K_2^{V^2} \cdot Y02^2 + K_1^V K_2^V \cdot Y02 \cdot Y03 \\ & + K_1^V K_2^V \cdot Y02 \cdot Y03 \cdot Y04 - K_2^{V^2} \cdot Y02^2 \cdot Y05 - PK_1^V \cdot Y01 \cdot Y03^2 = 0 \end{aligned} \quad (I.11)$$

The solution of equation I.11 could be substituted

into equation I.10 for calculation of α_V . The values of α_V and β_V are then used to calculate the values of mole fractions at chemical equilibrium from the relationships given in the Table I.3.

(11.4)

$$-0.134 \times 10^2 \left(\frac{1}{q} - \frac{1}{103.7} \right)$$

(11.4)

(11.5)

(11.6)

The reaction of formaldehyde in the
 at the temperature, Y_{H_2O} the
 in equilibrium with Y_{H_2O} and
 formaldehyde and the
 in the

APPENDIX II VAPOUR-LIQUID EQUILIBRIUM DATA FOR
FORMALDEHYDE-WATER SYSTEM

An algebraic set of equations was developed by Olsson and Svensson (73) for estimation of the vapour-liquid equilibrium data for the formaldehyde-water system. The equations are as follows:

$$XO1 = \frac{\frac{WO1}{30}}{\frac{WO1}{30} + \frac{(1-WO1)}{18}} \quad (II.1)$$

$$YO = \frac{0.4462.XO1.(0.7649+XO1)}{0.4462.XO1.(0.7649+XO1)+(1-XO1)(0.1448+XO1)} \quad (II.2)$$

$$AO = \ln\left(\frac{YO}{1-YO}\right) \quad (II.3)$$

$$A = AO - (1686. + 3013.XO1 - 6184.XO1^2) \left(\frac{1}{T} - \frac{1}{393.2}\right) \quad (II.4)$$

$$YO1 = \frac{\exp A}{1 + \exp A} \quad (II.5)$$

$$UO1 = \frac{30.YO1}{30.YO1 + 18(1-YO1)} \quad (II.6)$$

where WO1 is the weight fraction of formaldehyde in the liquid phase. T, the absolute temperature, YO1 the vapour phase mole fraction in equilibrium with XO1 the liquid phase mole fraction of formaldehyde and UO1 the weight fraction of the formaldehyde in the vapour.

Equations II.1 to II.6 could be used to calculate isothermal equilibrium data for the formaldehyde-water system. It is reported that (73) the values calculated through these equations show good agreement with the experimental results down to 60°C presented by Credali et al. (71).

Equations II.7 to II.11 can be used to calculate the isobaric vapour-liquid equilibrium data.

$$z = 3 + \ln \frac{P}{0.9869} \quad (\text{II.7})$$

$$t1 = 32.82451 + 17.68082 \cdot z + 1.319268 \cdot z^2 + 0.01990538 \cdot z^3 + 0.01672246 \cdot z^4 \quad (\text{II.8})$$

$$t2 = 132.83 - 31.816 \cdot W01 + 112.25 \cdot W01^2 - 234.08 \cdot W01^3 + 195.27 \cdot W01^4 \quad (\text{II.9})$$

$$t3 = 100.0 - 11.476 \cdot W01 + 44.019 \cdot W01^2 - 77.496 \cdot W01^3 + 61.320 \cdot W01^4 \quad (\text{II.10})$$

$$t = t3 + \frac{(t1 - 100.) (t2 - t3)}{32.9} \quad (\text{II.11})$$

where P is the system pressure in atmospheres and t the temperature in °C.

A computer program based on these equations was used

to calculate the isobaric vapour-liquid equilibrium data for the formaldehyde-water system.

Initial equilibrium

are needed

relationships based on estimated

and entropy of formation

relation.

reaction constant and

relation.

(III.6)

in the form of equation and

calculated from equation (III.4).

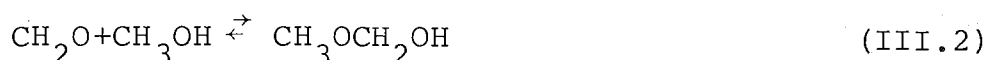
(III.4)

the free energy of

of the

APPENDIX III CHEMICAL EQUILIBRIUM CONSTANTS

The reaction constants for the chemical equilibrium of formaldehyde in the following reactions are needed for both the liquid and vapour phases.



The values for the reaction constants are reported in the literature (41,53) with the exception of the liquid phase reaction of formaldehyde with the methanol to produce hemiformal. This value was calculated from rigorous thermodynamic relationships based on estimated data for free energy, enthalpy and entropy of formation for the components in the reaction.

The relationship between the reaction constant and temperature is given by the equation III.3.

$$\frac{\partial \ln K}{\partial T} = \frac{\Delta H_R^\circ}{RT^2} \quad (\text{III.3})$$

The relationship between the reaction constant and the free energy of the reaction is given by equation (III.4).

$$\Delta G^\circ = RT \ln K \quad (\text{III.4})$$

where K is the reaction constant, T the temperature, ΔG° and ΔH_R° are the standard free energy and heat of the

reaction at one atmosphere.

The integration of equation III.3 between the temperatures 298 and T results in equation III.5.

$$\log K_T - \log K_{298} = \frac{-\Delta H_R^{\circ}}{2.303R} \left(\frac{1}{T} - \frac{1}{298} \right) \quad (\text{III.5})$$

The reaction constant at 298 K could be calculated from equation III.4, if the standard free energy of the reaction is known at this temperature. The value of ΔG_{298}° for hemiformal could be calculated using generalised estimation techniques. The value for formaldehyde in the liquid phase can be calculated using the value given for the vapour phase by Walker (41). Whilst ΔG_{298}° for methanol is well documented (165).

The standard free energy and heat of formation of hemiformal are calculated for the vapour phase, using the method described by Janz (169) as listed in Table III.1.

Table III.1

Component	ΔG_{298}° (kJ/mol)	ΔH_{298}° (kJ/mol)
$\text{CH}_3\text{OCH}_2\text{OH}(\text{g})$	-261.642	-352.303

The condensation of hemiformal can be analysed into three reversible stages:

1. Heating the vapour from 298 K to the normal boiling point, where the heat of vaporisation could be calculated.
2. Condensation of vapour at normal boiling point.
3. Cooling the liquid back to the 298 K.

ΔG_{298}° for the liquid hemiformal at the 298 K is obtained from the summation of ΔG° for the three steps.

The heat of vaporisation at normal boiling point is calculated using Nernst's equation (169) in the form of equation III.6, where DHV is the heat of vaporisation (J/mol) and T_b is the normal boiling point (°K).

$$\frac{DHV}{T_b} = 4.186(9.5 \log T_b - 0.007 T_b) \quad \text{(III.6)}$$

The normal boiling point of hemiformal has been calculated to be 326.9 K (Appendix IX). The heat of vaporisation at 326.9 K can be obtained by substituting into equation III.6 and this value can be extrapolated to 298 K, using the relationships given in Appendix IX. This value is calculated at 29.560 kJ/mol. The values of ΔS° for step 2 can be calculated by division of ΔH° by the normal boiling temperature. The values are listed in Table III.2.

Table III.2

	Enthalpy (kJ/mol)	Entropy [kJ/(mol.K)]
Step 1	ΔH_1^O	ΔS_1^O
Step 2	-29.560	-0.0904
Step 3	ΔH_3^O	ΔS_3^O

Assuming a constant heat of vaporisation the following relationships are obtained

$$\Delta H_1^O = -\Delta H_3^O \quad (\text{III.7})$$

$$\Delta S_1^O = -\Delta S_3^O \quad (\text{III.8})$$

The standard enthalpy and entropy of condensation of hemiformal at 298 K can be obtained from the summation of the enthalpy and entropy values.

$$\Delta H_{298}^O(\text{condensation hemiformal}) = -29.560 \text{ kJ/mol} \quad (\text{III.9})$$

$$\Delta S_{298}^O(\text{condensation hemiformal}) = -0.0904 \text{ kJ/mol K} \quad (\text{III.10})$$

The free energy of condensation at standard state can be calculated using equation III.11.

$$\Delta G^O(\text{condensation}) = \Delta H^O(\text{condensation}) - T\Delta S^O(\text{condensation}) \quad (\text{III.11})$$

Substitution of values from equations III.9 and III.10, with temperature at 298 K would result in equation III.12.

$$\Delta G_{298}^{\circ}(\text{condensation}_{\text{hemiformal}}) = -2.621 \text{ kJ/mol} \quad (\text{III.12})$$

A similar procedure can be applied for formaldehyde, where the heat of vaporisation for formaldehyde at the normal boiling point is given (41) as 23.316 kJ/mol.

$$\Delta G_{298}^{\circ}(\text{condensation}_{\text{formaldehyde}}) = -4.477 \text{ kJ/mol} \quad (\text{III.13})$$

The standard free energy of formation for the liquid phase can be calculated knowing the standard free energy of formation for the vapour phase and the standard free energy of condensation for each component from equation III.14.

$$\Delta G_{298}^{\circ}(\text{l}) = \Delta G_{298}^{\circ}(\text{g}) + \Delta G_{298}^{\circ}(\text{condensation}) \quad (\text{III.14})$$

The values are listed in Table III.3.

The standard free energy of the reaction in the liquid phase could be calculated from equation III.15.

$$\Delta G_{298}^{\circ}(\text{reaction}) = \Delta G_{298}^{\circ}(\text{CH}_3\text{OCH}_2\text{OH}_{\text{l}}) - \Delta G_{298}^{\circ}(\text{CH}_2\text{O}_{\text{l}}) - \Delta G_{298}^{\circ}(\text{CH}_3\text{OH}_{\text{l}}) \quad (\text{III.15})$$

Table III.3

Component	$\Delta G^{\circ}_{f,298}$ (kJ/mol)
CH ₂ O (g)	-109.949
(l)	-114.426
CH ₃ OCH ₂ OH (g)	-261.592
(l)	-264.213
CH ₃ OH (l)	-166.603

where

$$\Delta G^{\circ}_{298}(\text{reaction}) = 16.816 \text{ kJ/mol} \quad (\text{III.16})$$

The enthalpy of the reaction for the vapour phase can be calculated at this temperature from the definition of the reaction constant using a similar procedure used to that of Walker (41) for the calculation of the heat of the reaction. This value was calculated at -61.283 kJ/mol. The heat of reaction in the liquid phase can be calculated from equation III.17, knowing the heat of vaporisation for the components at 298 K.

$$\begin{aligned} \Delta H^{\circ}_{298}(\text{reaction}_l) = & \Delta H^{\circ}_{298}(\text{reaction}_g) + \Delta H^{\circ}_{298}(\text{vaporisation, hemiformal}) \\ & - \Delta H^{\circ}_{298}(\text{vaporisation, formaldehyde}) - \Delta H^{\circ}_{298}(\text{vaporisation, methanol}) \end{aligned} \quad (\text{III.17})$$

The heat of vaporisation for hemiformal was calculated

earlier. The heat of vaporisation for formaldehyde at 298 K has been calculated from the value given by Walker at 254 K and extrapolating this value to 298 K using the relationships given in Appendix IX. The heat of vaporisation for methanol has been also calculated from the relationship in Appendix IX. Substitution of the heat of reaction and heats of vaporisation of the components into equation III.17, would result in equation III.18.

$$\Delta H_{298}^{\circ}(\text{reaction}_\ell) = -33.783 \text{ kJ/mol} \quad (\text{III.18})$$

The reaction constant at 298 K can be calculated from equation III.4, knowing the value of $\Delta G_{298}^{\circ}(\text{reaction})$. This value is given by equation III.19.

$$K_{298}^L = 885.115 \quad (\text{III.19})$$

Integrating equation III.3 and substituting the value of K_{298}^L into the integrated form of equation III.3 would result in equation III.20.

$$\log K_2^L = -2.97 + \frac{1763.64}{T} \quad (\text{III.20})$$

Equation III.20 is similar in form to those of the reported reaction constants for the reaction of formaldehyde with water and methanol as illustrated by equation III.21.

$$\log K = A + \frac{B}{T} \quad (\text{III.21})$$

The constants A and B are listed for all the reactions in Table III.4.

Table III.4

Type of reaction	Phase	A	B	Source
1	vapour	9.8	-3200.0	(53)
	liquid	3.06	-2079.23	(43)
2	vapour	8.2	-3200.0	(53)
	liquid	-2.97	1763.64	calculated

where

$$K_1^V = \frac{P Y_{H_2O} Y_{CH_2O}}{Y_{CH_2(OH)_2}} \quad (III.22)$$

$$K_1^L = \frac{X_{CH_2O}}{X_{CH_2(OH)_2}} \quad (III.23)$$

$$K_2^V = \frac{P Y_{CH_3OH} Y_{CH_2O}}{Y_{CH_3OCH_2OH}} \quad (III.24)$$

$$K_2^L = \frac{X_{CH_3OCH_2OH}}{X_{CH_3OH} X_{CH_2O}} \quad (III.25)$$

APPENDIX IV.1 LIQUID PHASE VISCOSITY

The viscosity of pure liquids can be related to temperature. Several generalised techniques have been proposed for the estimation of liquid viscosity (158). Arrhenius's and Thomas's equations (165) were used to calculate the viscosity of components. The error of estimation is less than 30 percent.

$$\epsilon_{Lb} = 0.000275 (\rho_{Lb})^{\frac{1}{2}} \quad (IV.1)$$

$$\epsilon_L = 0.1167 \rho_L^{\frac{1}{2}} 10^{\gamma-3} \quad (IV.2)$$

where
$$\gamma = \frac{C(1-T_r)}{T_r} \quad (IV.3)$$

The viscosity ϵ_L is expressed in Nsm^{-2} and ρ the density in gcm^{-3} equivalent to 1000 kgm^{-3} . The normal boiling point is denoted by the subscript b. The constant C is calculated from the calculation of group contribution in the molecule.

The dependence of viscosity on temperature is correlated with an accuracy of 2 percent with the equation of Guzman-Andrade (165) as illustrated by equation IV.4.

$$\epsilon_L = A e^{B/T} \quad (IV.4)$$

The viscosity of formaldehyde was calculated at its boiling point and at -80°C . The density of formaldehyde has been reported at these temperatures by Walker (41).

The viscosity of hemiformal was calculated at its boiling point and at 298 K using equations IV.1 and IV.2. A similar procedure was applied for the calculation of the viscosity of methylene glycol. The values of density for each component have been calculated in Appendix V.2.

The constants A and B in equation IV.4 were calculated for all the components using the two known values. The values of A and B for water and methanol have been reported by Perry (165). These constants are listed in Table IV.1.

Table IV.1

Component	A	B
Formaldehyde	17.249×10^{-6}	674.403
Hemiformal	106.578×10^{-6}	292.066
Methanol	9.195×10^{-6}	1219.206
Methylene glycol	65.494×10^{-6}	677.892
Water	1.791×10^{-6}	1851.68

No reliable method has yet been suggested for the estimation of liquid mixtures viscosity. Usually a power series, in terms of the viscosity of the components of the mixture has been suggested (158). Therefore a power series in the form of equation IV.5 has been introduced for the calculation of the mixture viscosity. The constants of equation IV.5 have been estimated using

the experimental data of Walker. The constants were estimated using Marquardt's (225) regression algorithm.

$$\epsilon_{Lmix}^a = b + c.X1.\epsilon_{L1}^a + d.X2.\epsilon_{L2}^a + e.X3.\epsilon_{L3}^a + f.X4.\epsilon_{L4}^a + g.X5.\epsilon_{L5}^a \quad (IV.5)$$

The variable X1 to X5 and ϵ_{L1} to ϵ_{L5} are the mole fractions and viscosities of formaldehyde to water. The constants are illustrated in equation IV.6.

$$\epsilon_{Lmix} = (0.1618 - 69.9404.X1.\epsilon_{L1}^{0.1661} - 13.6794.X2.\epsilon_{L2}^{0.1661} + 3.1316.X3.\epsilon_{L3}^{0.1661} + 1.3178.X4.\epsilon_{L4}^{0.1661} + 0.8737.X5.\epsilon_{L5}^{0.1661}) \times 10^{-3} \quad (IV.6)$$

A very good fit was obtained with an error of less than 5 percent.

APPENDIX IV.2 VAPOUR PHASE VISCOSITY

The viscosity of a pure component in the vapour phase was calculated using the rigid sphere model (158).

$$\epsilon_{Gi} = 0.2669 \times 10^{-5} \frac{(MT)}{\sigma^2 \Omega_V} \quad (IV.7)$$

where

$$\epsilon_{Gi} = \text{viscosity of pure component } i \text{ in vapour phase} \quad (Ns m^{-2})$$

$$T = \text{absolute temperature} \quad (K)$$

$$\sigma = \text{collision diameter} \quad (\text{Angstrom})$$

Ω_V = collision integral

π = potential parameter

V_C = critical volume

M = molecular weight

$$\text{and } \sigma = 0.833 V_C^{1/3} \quad (\text{IV.8})$$

The values of Ω_V for the Lennard Jones and Stockmayer potential functions (158) are calculated from a correlation fitted to the data reported by Bromley and Wilke (161) and Hirschfelder, Curtiss and Bird (163). The correlation is given by equation IV.9.

$$\Omega_V = 1.1718 + 2.8657 e^{-1.9377 \left(\frac{TK}{\pi} \right)} \quad (\text{IV.9})$$

$$\frac{\pi}{K} = 1.39 T_b \quad (\text{IV.10})$$

where T_b is the normal boiling point and T the temperature in K.

The viscosity of multicomponent gas mixture may be calculated by the rigorous kinetic theory (164) in the form of equation IV.11.

$$\epsilon_{Vmix} = \frac{\sum_{i=1}^m \epsilon_{Gi}}{\left[1 + \sum_{\substack{j=1 \\ j \neq i}}^m \phi_{ij} \left(\frac{Y_j}{Y_i} \right) \right]} \quad (\text{IV.11})$$

$$\text{where } \phi_{ij} = \left[1 + \left(\frac{\epsilon_{G,i}^{1/2} M_i^{1/4}}{\epsilon_{G,j}^{1/2} M_j^{1/4}} \right)^2 \right] / \left\{ \sqrt{8} \left[1 + \left(\frac{M_i}{M_j} \right)^{1/2} \right] \right\} \quad (\text{IV.12})$$

ϵ_{Vmix} = viscosity of the gas mixture (Nsm^{-2})

M_i and M_j = molecular weight

APPENDIX IV.3 LIQUID PHASE DIFFUSIVITY

The liquid phase diffusivity can be estimated from the correlation given by Wilke and Chang (248) in the form of equation IV.13.

$$\frac{DL_i}{T} \epsilon_{Lmix} = 7.4 \times 10^{-5} \frac{(XM)}{V_{bi}^{0.6}} \quad (IV.13.)$$

where DL_i = diffusivity of solute at infinite dilution
($\text{cm}^2 \text{s}^{-1}$)

X = association factor (taken as unity for the mixture)

M = average solvent molecular weight

V_{bi} = molar volume of solute at normal boiling point
($\text{cm}^3 \text{mol}^{-1}$)

ϵ_{Lmix} = solution viscosity (Nsm^{-2})

T = absolute temperature

The molar volume of solute at boiling point is calculated in Appendix V.2.

APPENDIX IV.4 VAPOUR PHASE DIFFUSIVITY

The values of the vapour phase diffusivity can be calculated by the correlation of Wilke and Lee (155) in the form of equation IV.14 for any binary pair.

$$DG_{12} = \frac{BT^{3/2} \sqrt{(1/M_1) + (1/M_2)}}{P \sigma_{12}^2 I_D} \quad (IV.14)$$

$$\text{where } B = [10.7 - 2.46\sqrt{(1/M_1) + (1/M_2)}] \cdot 10^{-4} \quad (\text{IV.15})$$

T = temperature (K)

M_1 and 2 = molecular weight of components 1 and 2

P = absolute pressure (atm)

σ_{12} = collision diameter (Angstrom)

$$\sigma_{12} = \frac{(\sigma_o)_1 + (\sigma_o)_2}{2} \quad (\text{IV.16})$$

$$\sigma_o = 1.18 V_b^{1/3} \quad (\text{IV.17})$$

V_b = molar volume at normal boiling point (cm^3/mol)

I_D = collision integral for diffusion, a function of KT/π_{12}

$$\frac{\pi_{12}}{K} = \sqrt{\left(\frac{\pi_1}{K_1}\right) \left(\frac{\pi_2}{K_2}\right)} \quad (\text{IV.18})$$

K = Boltzman constant = 1.38×10^{-6} (erg K^{-1})

π_{12} = energy of molecular interaction (erg)

$$\frac{\pi}{K} = 1.15 T_b \quad (\text{IV.19})$$

T_b = normal boiling point.

The value of I_D can be calculated as a function of KT/π_{12} from a correlation derived from the data represented by

Hirschfelder, Bird and Spotz (156). The correlation is obtained by fitting the model to the data represented in a table form (156).

$$I_D = 0.5578 + 1.4574 e^{-2.2137 \left(\frac{KT}{\pi_{12}} \right)} \quad (IV.20)$$

The diffusion of a component in a mixture can be determined from equation IV.21 (157).

$$DG_i = \frac{1 - Y_i}{\sum_{\substack{j=1 \\ j \neq i}}^m \frac{Y_j}{DG_{ij}}} \quad (IV.21)$$

where DG_i = gas diffusivity of the i th component in a mixture

Y_i = mole fraction of component i .

(7.1)

... in K. The ... water refraction ... efficient B depends ... is grouped under ... B is reported at 16300. The ... are calculated at ... constitution of these ... would result in the normal ... at 326.3 K.

... of the components ...

APPENDIX V.1 CRITICAL PROPERTIES

The experimental critical properties of formaldehyde hemiformal and methylene glycol have not been reported in the literature. These values would have to be estimated using generalised estimation techniques.

In order to estimate the critical properties, knowledge of the normal boiling temperature is required. The normal boiling point of formaldehyde and methylene glycol could be found in literature (41, 220). However the normal boiling point of hemiformal will have to be estimated using generalised techniques.

The normal boiling point of hemiformal was estimated using Meissner's equation (165).

$$T_b = \frac{637 (RD)^{1.47} + B}{(p)} \quad (V.1)$$

Where T_b is the normal boiling point in K. The coefficients (RD) and (p) are additive molar refraction and parachor of the molecule. The coefficient B depends on the type of molecule. Hemiformal is grouped under alcohols where the value of B is reported at 16500. The value of (RD) and p for hemiformal are calculated at 14.604 and 150.8 respectively. Substitution of these values into equation V.1 would result in the normal boiling temperature of hemiformal at 326.9 K.

The normal boiling points of the components are

listed in Table V.1.

Table V.1

Component	Normal boiling point K
Formaldehyde	253.4
Hemiformal	326.9
Methylene glycol	460.0

The critical temperature of the components are estimated by summation of the additive contribution method of Eduljee (165). Using the normal boiling temperature.

$$T_c = \frac{T_b}{\Sigma \Delta T / 100} \quad (V.2)$$

where T_c is the critical temperature and $\Sigma \Delta T$ the sum of contribution of each atom in the molecule.

The critical pressure is also calculated using the Eduljee (165) method.

$$P_c = \frac{10^4 M}{(\Sigma \Delta p)^2} \quad (V.3)$$

where P_c the critical pressure is calculated in atmospheres which is equivalent to 101.32 kN m^{-2} , M the molecular weight and $\Sigma \Delta p$ are the additive contribution of atoms in the molecule.

The critical volume is calculated using Benson's relation (158).

$$V_c = V_b (0.422 \log P_c + 1.981) \quad (V.4)$$

where V_b is the molar liquid volume at normal boiling point in cm^3/mol which is equivalent to $0.001 \text{ m}^3/\text{kmol}$. The value of V_b for hemiformal and methylene glycol are calculated using the additive contribution of the atoms in a molecule (165). The values of V_b are listed in Table V.2 for the components, where the value of V_b for formaldehyde is reported by Walker (41).

Table V.2

Component	$V_b (\text{cm}^3/\text{mol})$
Formaldehyde	36.80
Hemiformal	69.1
Methylene glycol	44.4

The estimated critical properties are listed in

Table V.3

Table V.3

Component	$T_c (\text{K})$	$P_c (\text{atm})$	$V_c (\text{cm}^3/\text{mol})$
Formaldehyde	419.2	121.4	79.8
Hemiformal	472.7	58.2	182.9
Methylene glycol	630.5	96.7	103.5

The values for methanol and water are reported by Prausnitz, Eckert, Orye and O'Connell (191).

APPENDIX V.2 LIQUID MOLAR VOLUME

The liquid molar volume is required at three different temperatures. Since the values of the liquid molar volume are known at the normal boiling temperature, these values can then be extrapolated to other temperatures using equation V.5 (158).

$$\frac{(\rho_L - \rho_V)^2}{(\rho_L - \rho_V)^1} = \left(\frac{T_c - T_2}{T_c - T_1} \right)^{1/3} \quad (V.5)$$

where ρ_L and ρ_V are the liquid and vapour densities at temperatures 1 and 2. The value of ρ_L is much larger than ρ_V where the latter could be neglected in the equation. The values of the liquid molar volume are listed in Table V.4 for the components.

Table V.4

Component	T_1 (K)	V_1 (cm ³ /mol)	T_2 (K)	V_2 (cm ³ /mol)	T_3 (K)	V_3 (cm ³ /mol)
Formaldehyde	200.0	33.5	220.0	34.6	253.0	36.8
Hemiformal	273.0	62.2	298.0	65.1	326.9	69.1
Methylene glycol	273.0	42.6	298.0	43.6	460.0	44.4

The values for methanol and water can be found in literature (191).

APPENDIX V.3 VAPOUR PRESSURE DATA

The vapour pressure data of the components were fitted to the extended Antoine equation in the form of equation V.6. The parameters of this equation were estimated using program VAPFIT as developed by Prausnitz et al (191).

$$\ln P(\text{atm}) = C_1 + \frac{C_2}{C_3 + T} + C_4 T + C_5 T^2 + C_6 \ln T \quad (\text{V.6})$$

The vapour pressure data for formaldehyde has been reported by Walker (41) and the data were applied to program VAPFIT to estimate the parameters C_1 to C_6 .

The experimental vapour pressure data for hemiformal has not been reported in the literature. In order to evaluate the vapour pressure data for hemiformal, the phase equilibria relationships simplified to the limits, were used. Large errors in vapour pressure data of hemiformal may be caused by this assumption. Serious investigation is needed in order to evaluate accurate data for the vapour pressure of hemiformal.

The simplified form of phase equilibria equation is obtained by assuming ideal vapour and liquid phases.

$$P_i^O = \frac{Y_i P}{X_i} \quad (\text{V.7})$$

The multicomponent data represented by Walker was used to calculate the vapour pressure data of hemiformal. Some

of the data are listed in Table V.5.

Table V.5

T (K)	Vapour pressure (atm)
326.9	1.0
345.5	1.137
347.8	1.442
350.6	1.800
353.8	2.445
357.6	3.528
361.8	5.681
366.8	8.992

These data were then applied to program VAPFIT to estimate the coefficients of equation V.6.

The vapour pressure data of methylene glycol has been reported by Chueh (220). These data were found to result in large deviations in the phase and chemical equilibria calculations. However, the vapour pressure data at the boiling point and temperatures close to the boiling point were found to be satisfactory. Therefore the Clausius Clapeyron equation was used to calculate the vapour pressure data based on the values of vapour pressure in the boiling point region. The modified Clausius Clapeyron equation applied to the vapour pressure is

illustrated in equation V.8.

$$\frac{dP}{P} = \frac{\Delta H}{RT^2} dT \quad (V.8)$$

where P is the vapour pressure at temperature T and ΔH is the heat of vaporisation which is a function of temperature. The value of ΔH can be found at the boiling point region using the Watson's equation (169).

$$\frac{\Delta H_1}{\Delta H_2} = \left(\frac{1-T_{r1}}{1-T_{r2}} \right)^{0.38} \quad (V.9)$$

where ΔH is calculated at reduced temperatures of T_{r1} and T_{r2} . The heat of vaporisation can be estimated if two vapour pressure data are available using the Watson's estimation equation (169).

$$\Delta H = 7.8983 B \left(\frac{T_b}{T_b - 43} \right)^2 \quad (V.10)$$

$$B = \frac{\ln \left(\frac{P_2}{P_1} \right)}{\frac{1}{T_1 - 43} - \frac{1}{T_2 - 43}} \quad (V.11)$$

where ΔH is calculated in J/mol, using the vapour pressures P_1 and P_2 .

The values of P and T were obtained from the correlation represented by Chueh (220) for methylene glycol.

Table V.6

No.	P (atm)	T (K)
1	1.0	460.0
2	0.9244	451.0

The values from Table V.6 are applied to equation V.10 and V.11. The resulting heat of vaporisation is then applied to equation V.9 resulting in equation V.12.

$$\Delta H = 23489.85 (1 - 0.001586 T)^{0.38} \quad (V.12)$$

Equation V.12 can be substituted into equation V.8. The integration of equation V.8 would result in a correlation for producing vapour pressure data at different temperatures. Some of the data are listed in Table V.7.

Table V.7

T (K)	P (atm)
378.0	0.4027
383.0	0.4319
388.0	0.4621
393.0	0.4934
398.0	0.5257
403.0	0.5590
408.0	0.5933
413.0	0.6286

The data is then applied to program VAPFIT to estimate the coefficients of equation V.6. The results are listed in Table V.8 for the components. The values for methanol and water have been reported by Prausnitz et al (191).

Table V.8

Component	C_1	C_2	C_3	C_4	C_5	C_6
Formaldehyde	216.4883	- 7321.2118	0.0	0.0806	0.0	- 37.5809
Hemiformal	-1014.5225	99204.1567	0.0	0.6342	0.0	87.0
Methylene glycol	2809.6056	-92977.6579	0.0	0.5955	0.0	-470.0

The acentric factor for the components was also calculated by VAPFIT and are listed in Table V.9. The acentric factor of the homomorph of the molecules was determined by the shape of the molecule. Since the shape of the molecules of formaldehyde, hemiformal and methylene glycol are similar to that of acetaldehyde, the acentric factor of the homomorph of acetaldehyde was used for these components.

The association factor for the components with the exception of methanol and water, are set equal to zero since the accurate information was not available for the association of pure components. Therefore it was assumed

that the components do not associate with their own molecules. This assumption however does not affect the accuracy of calculations, since the effect of vapour phase nonideality is minimal.

Table V.9

Component	ω	ω_H
Formaldehyde	0.365	0.152
Hemiformal	0.808	0.152
Methylene glycol	1.22	0.152

APPENDIX V.4 PARTIAL MOLAR VOLUME

The knowledge of the partial molar volumes of the supercritical component in the condensable components is required for the vapour-liquid equilibrium calculations for a supercritical component. The partial molar volumes of formaldehyde in hemiformal, methanol, methylene glycol and water were calculated at different temperatures, using the estimation methods represented by Lyckman, Eckert and Prausnitz (168, 242). The general form of the equation for the estimation of partial molar volumes is given by equation V.13.

$$\frac{v_2^P c_2}{RT_{c2}} = f_1 \left(\frac{P_{c2} T}{C_1 T_{c2}} \right) \quad (V.13)$$

where

f_1 = a universal function

v_2 = partial molar volume of the light component in liquid solution

P_{c2} = critical pressure of light component

T_{c2} = critical temperature of light component

T = temperature of solution

R = gas constant

$C_1 = \frac{\Delta \bar{u}_1}{V_1}$ cohesive energy density of the heavy component

$\Delta \bar{u}_1$ = energy of vaporisation (to zero pressure) of solvent at T

V_1 = molar liquid volume of solvent at T .

The cohesive energy density is calculated using the method suggested by Lyckman, Eckert and Prausnitz (168) in the form of equation V.14

$$\frac{\delta}{P_c^{1/2}} = f_2(T_r, \omega) \quad (V.14)$$

where

$$\delta = \left(-\frac{\Delta u}{V} \right)^{1/2} \text{ solubility parameter} \quad (V.15)$$

ω = acentric factor

T_r = reduced temperature

$$f_2 = \delta R(0) + \omega \delta R(1) + \omega^2 \delta R(2) \quad (V.16)$$

The values of $\delta R(0)$ to $\delta R(2)$ can be found from tables as a function of temperature(168,242). The values of T_r

was chosen at 0.5, 0.55 and 0.6 where the corresponding values of $\delta R(0)$ to $\delta R(2)$ could be obtained from a tabulated form (242). The acentric factors are then used to calculate the value of δ at the corresponding temperatures for formaldehyde in all the other components. The value of C is then calculated followed by the calculation of the group $\frac{P_{c2} T}{C_1 T_{c2}}$ which was then used to obtain the value of $\frac{v_2 P_{c2}}{R T_{c2}}$ from the function f_1 which was represented as a graph (168). The calculated values are represented in the Table V.10.

Table V.10

System	T (K)	v (cm ³ mol ⁻¹)
Formaldehyde-hemiformal	236.3	27.20
	259.9	27.20
	283.6	27.21
Formaldehyde-methanol	256.6	27.20
	282.3	27.20
	307.9	27.20
Formaldehyde-methylene glycol	315.2	27.19
	346.8	27.17
	378.3	27.19
Formaldehyde-water	323.7	27.17
	356.1	27.19
	388.4	27.19

APPENDIX V.5 HEAT CAPACITIES

The heat capacities were estimated for the vapour phase as a function of temperature for formaldehyde, hemiformal and methylene glycol. The relationships for the heat capacities of methanol and water are well documented and can be found in the literature (165). The vapour phase heat capacities of methanol and water were also calculated from the generalised techniques and compared with the reported values and an average error of less than 3 percent was achieved.

The estimation is based on the generalised technique represented by Janz (169). The generalised vibrational frequencies for the stretching and bending modes of each valence bond were calculated and applied with additive contribution of the atoms and bonds of the molecule. The resulting relationship is in the general form of equation V.17.

$$C_p = Ch_1 + Ch_2.T + Ch_3.T^2 \quad (V.17)$$

The coefficients Ch_1 , Ch_2 and Ch_3 are listed in Table V.11 for the components.

The values of heat capacities are calculated in $Jmol^{-1}K^{-1}$. The temperature is in K.

Table V.11

Component	Ch1	Ch2	Ch3
Formaldehyde	29.034	39.725×10^{-3}	-2.667×10^{-6}
Hemiformal	30.401	172.580×10^{-3}	-62.840×10^{-6}
Methanol	25.608	85.168×10^{-3}	-23.885×10^{-6}
Methylene glycol	29.817	125.530×10^{-3}	-53.062×10^{-6}
Water	25.024	38.118×10^{-3}	-14.107×10^{-6}

APPENDIX V.6 ENTHALPY

In order to calculate the enthalpy of the liquid, the value of the heat of vaporisation at the temperature of the calculation is required. The enthalpy of liquid could be calculated by subtraction of the heat of vaporisation from the enthalpy of the vapour at the same temperature.

The heat of vaporisation can be extrapolated using the Watson's equation (169) in the form of equation V.18.

$$\frac{\Delta H_1}{\Delta H_2} = \left(\frac{1-T_{r1}}{1-T_{r2}} \right)^{0.38} \quad (V.18)$$

where ΔH and T_r are the heat of vaporisation and reduced temperature at points 1 and 2. In order to use this equation the heat of vaporisation should be known at least one temperature. The heat of vaporisation at normal

boiling point is estimated using the Watson's estimation equation (169) in the form of equation V.19.

$$\Delta H = 7.898313 \left(\frac{T_b}{T_b - 43} \right)^2 \quad \text{(V.19)}$$

T_b = normal boiling point

$$B = \ln P_2/P_1 / \left[\left(\frac{1}{T_1 - 43} \right) - \left(\frac{1}{T_2 - 43} \right) \right] \quad \text{(V.20)}$$

where P and T are the vapour pressure and temperature at points 1 and 2. The expression for vapour pressure is used to calculate the vapour pressure at two arbitrary temperatures for hemiformal and methylene glycol. The heat of vaporisation and vapour pressure for formaldehyde, methanol and water can be found in literature (41,165). The heat of vaporisation for components are given in equations V.21 - V.25.

$$\Delta H_1 = 33197.575 \left(1 - \frac{T}{419.24} \right)^{0.38} \quad \text{(V.21)}$$

$$\Delta H_2 = 31714.170 \left(1 - \frac{T}{472.66} \right)^{0.38} \quad \text{(V.22)}$$

$$\Delta H_3 = 51565.835 \left(1 - \frac{T}{513.2} \right)^{0.38} \quad \text{(V.23)}$$

$$\Delta H_4 = 26341.711 \left(1 - \frac{T}{630.48} \right)^{0.38} \quad \text{(V.24)}$$

$$\Delta H_5 = 55280.496 \left(1 - \frac{T}{647.4} \right)^{0.38} \quad \text{(V.25)}$$

The values of ΔH are in Jmol^{-1} and temperature in K.

APPENDIX VI

COMPUTER PROGRAMS FOR VAPOUR-LIQUID
EQUILIBRIUM

Listing of the programs for vapour liquid equilibria accompanied with a chemical reaction are given in this appendix. The listing includes the following segments;

1. Subroutine RSTATE
2. Subroutine ACTCO
3. Subroutine PHIMIX
4. Subroutine VIRIAL
5. Subroutine INPUT (Version A)
6. Subroutine OUTPUT
7. Subroutine MODCON
8. Subroutine BUBLDILF (Version A)
9. Program SD

SUBROUTINE RSTATE

SUBROUTINE FOR CALCULATION OF STANDARD STATE PROPERTIES

```

DIMENSION TITLE(12), TCRIT(6,6), PCRT(6,6), VCRIT(6),
1 OMEGA(6), IDENT(6,2), VLIQ(6), CVLIQ(6,3), PSAT(6),
2 CPSAT(6,6), CACTCO(6,6,3), GAMMA(6), X(10,10), Y(10), PHI(6),
4 CHENRY(10,6,2), VLIQL(10,6), CVLIQL(10,6,2), OMEGAH(6),
3B(6,6), F(6), FREFER(6), NREFER(6), HENRY(10,6)
DIMENSION DIPOLE(6), ETA(6), X1(10)
COMMON/SAI1/TITLE, NCOMP, NLIGHT, NACTCO, TCRIT, PCRT, VCRIT, OMEGA
COMMON/SAI2/IDENT, VLIQ, CVLIQ, PSAT, CPSAT, CACTCO, GAMMA, X, SUMX, Y
COMMON/SAI3/SUMY, P, T, TOLD, PHI, B, BMIX, VMIX, ZMIX, F, FREFER, NREFER
COMMON/SAI4/HENRY, CHENRY, VLIQL, CVLIQL, OMEGAH, DIPOLE, ETA, NCRIT, X1

```

FUNCTION STATEMENTS

```

VAPRESF(TR, OMEG) = EXP(2.3025 * ((((-0.3456/TR + 1.454)/TR
1 -4.318)/TR + 3.209) + OMEG * (((0.3981/TR - 2.524)/TR + 2.008)/
2 TR + 0.1175)))
FSATOF(TR) = (-1.1970522/TR - 1.3785023)/TR + 2.0048841
FSAT1F(TR) = (-2.7741817/TR + 1.5454928)/TR + 1.3057555
PHISOFT(TR) = ((0.57335015/TR - 3.076574)/TR + 5.6085595)/TR
1 -3.5021358
PHIS1F(TR) = (((((((0.012089114/TR - 0.015172164)/TR
1 -0.068603516)/TR + 0.024364816)/TR + 0.14936906)/TR + 0.1892703
2 7)/TR - 0.12147436)/TR - 0.10665730)/TR - 1.1662283)/TR
3 + 0.12666184)/TR + 0.3166137)/TR + 4.3538729)/TR - 3.7694018
DELOF(TR) = (((-20.141089 * TR + 57.150420) * TR - 60.717499) * TR
1 + 27.093334) * TR - 3.1509051
DEL1F(TR) = (((-52.996350 * TR + 151.56585) * TR - 153.64561) * TR
1 + 59.821527) * TR - 4.3229852
DEL2F(TR) = (((-6.8437885 * TR + 8.6363569) * TR + 32.902287) *
1 TR - 89.695653) * TR + 73.721696) * TR - 18.674318
VOLINDF(A) = (-9.5259777 * A + 2.9766410) * A + 0.085762954

```

A EQUALS T*PC/(TC*COHESIVE ENERGY DENSITY) PC HAS UNITS OF CAL/C

```

N1 = NLIGHT + 1
IF (T - TOLD) 290, 381, 290
290 RT = 82.057 * T

```

CALCULATE THE REFERENCE FUGACITY AND LIQUID VOLUME OF ALL COMPONENTS
BELOW THEIR CRITICAL POINT, AND NOTE SUPERCRITICAL COMPONENTS

```

NCRIT = NLIGHT
DO 380 J = N1, NCOMP
TR = T / TCRIT(J,J)
W = OMEGA(J)

```

```

      IF (TR = 1.0) 295, 295, 370
295 IF (CPSAT(J,1)) 300, 310, 300
3000 PSAT(J) = EXP(CPSAT(J,1) * CPSAT(J,2) / (CPSAT(J,3) * T + CPSAT(J,4) * T *
      1 CPSAT(J,5) * T**2 + CPSAT(J,6) * ALOG(T))
      GO TO 320
310 PSAT(J) = PCRT(J,J) * VAPRESF(TR, W)
320 IF (TR = 0.56) 330, 330, 340
330 PHIS = EXP(B(J,J) * PSAT(J) / RT)
      GO TO 360
340 PHIS = EXP(PHISOF(TR) * W * PHIS1F(TR))
360 VLIQ(J) = CVLIQ(J,1) + CVLIQ(J,2) * T + CVLIQ(J,3) * T**2
      FREFER(J) = PSAT(J) * PHIS * EXP(-VLIQ(J) * PSAT(J) / RT)
      GO TO 380
370 NCRIT = J
380 CONTINUE

C
C CHECK TO DETERMINE IF ANY SUPERCRITICAL COMPONENTS EXIST
C
381 IF (NCRIT) 430, 430, 382
382 VOLSUM = 0.0
      NCRIT1 = NCRIT + 1
      DO 383 J = NCRIT1, NCOMP
      VOLSUM = VOLSUM + X1(J) * VLIQ(J)
383 CONTINUE

C
C CALCULATE REFERENCE FUGACITIES OF NONCONDENSABLE COMPONENTS THAT ARE
C SLIGHTLY ABOVE CRITICAL TEMPERATURE AND TREATED AS HYPOTHETICAL
C LIQUIDS -- ALSO ESTIMATE THE PARTIAL MOLAR VOLUME AT INFINITE DILUTION
C FOR THESE SPECIES
C
      IF (NCRIT = NLIGHT) 385, 400, 385
385 DELSUM = 0.0
      DO 386 J = NCRIT1, NCOMP
      W = OMEGA(J)
      TR = T / TCRT(J,J)
      DEL = SQRT(PCRT(J,J) * (DELOF(TR) * W * DEL1F(TR) + W**2 * DEL2F(TR)))
      DELSUM = DELSUM + DEL * VLIQ(J) * X1(J)
386 CONTINUE
      IF (VOLSUM) 387, 387, 388
387 DELAVG = DEL
      GO TO 389
388 DELAVG = DELSUM / VOLSUM
389 DO 390 J = N1, NCRIT
      TR = T / TCRT(J,J)
      FREFER(J) = PCRT(J,J) * EXP(FSATOF(TR) * OMEGA(J) * FSAT1F(TR))
      VLIQ(J) = 82.057 * TCRT(J,J) * VOLINDF(TR * PCRT(J,J) / (41.298 *
      1 DELAVG **2)) / PCRT(J,J)
390 CONTINUE

C
C THE REFERENCE STATE FOR A SUPERCRITICAL COMPONENT TREATED IN THE
C UNSYMMETRIC CONVENTION IS THE HENRY'S CONSTANT OF THAT COMPONENT
C IN ITS REFERENCE SOLVENT -- ESTIMATE AVERAGE PARTIAL MOLAR VOLUME
C
      IF (NLIGHT) 430, 430, 400
400 DO 420 J = 1, NLIGHT
      VOL = 0.0
      DO 410 I = NCRIT1, NCOMP
      VLIQL(J,I) = CVLIQL(J,I,1) + CVLIQL(J,I,2) * T
      OHENRY(J,I) = CHENRY(J,I,1) * T**2 * CHENRY(J,I,2) * EXP(-VLIQL(J,I) * PSAT(I)
      1 / RT)
      VOL = VOL + X1(I) * VLIQ(I) * VLIQL(J,I)
410 CONTINUE
      NR = NREFER(J)
      FREFER(J) = HENRY(J,NR)
      VLIQ(J) = VOL / VOLSUM
420 CONTINUE
430 RETURN
      END

```

SUBROUTINE ACTCO

C
C
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C

CALCULATE ACTIVITY COEFFICIENTS FROM WILSON EQUATIONS
FOR BOTH SYMMETRIC AND UNSYMMETRIC CONVENTIONS.

ODIMENSION TITLE(12), TCRIT(6,6), PCRT(6,6), VCRIT(6),
1 OMEGA(6), IDENT(6,2), VLIQ(6), CVLIQ(6,3), PSAT(6),
2 CPSAT(6,6), CACTCO(6,6,3), GAMMA(6), X(10,10), Y(10), PHI(6),
4 CHENRY(10,6,2), VLIQL(10,6), CVLIQL(10,6,2), OMEGAH(6),
3B(6,6), F(6), PREFER(6), NREFER(6), HENRY(10,6)
DIMENSION DIPOLE(6), ETA(6), X1(10)
DIMENSION XLAMDA(30,30)
COMMON/SAI1/TITLE, NCOMP, NLIGHT, NACTCO, TCRIT, PCRT, VCRIT, OMEGA
COMMON/SAI2/IDENT, VLIQ, CVLIQ, PSAT, CPSAT, CACTCO, GAMMA, X, SUMX, Y
COMMON/SAI3/SUMY, P, T, TOLD, PHI, B, BMIX, VMIX, ZMIX, F, PREFER, NREFER
COMMON/SAI4/HENRY, CHENRY, VLIQL, CVLIQL, OMEGAH, DIPOLE, ETA, NCRIT, X1
IF (ABS(T-TOLD)-1.0E-05)55,55,1

1 RT = 1.9872*T
N1 = NLIGHT + 1

C
C
C

CALCULATION OF WILSON PARAMETER FOR INTERACTION OF NONCONDENSABLE

IF (NLIGHT)2,30,2

C
C
C
C

CALCULATION OF WILSON PARAMETERS FOR INTERACTION OF NONCONDENSABLE
COMPONENTS WITH THEIR REFERENCE SOLVENT, UNSYMMETRIC CONVENTION

2 DO 25 K = 1, NLIGHT
NR = NREFER(K)
XLAMDA(K,NR) = (VLIQ(NR)/VLIQL(K,NR))*EXP(-CACTCO(K,NR,1)/RT)
XLAMDA(NR,K) = 0.0

C
C
C
C

CALCULATION OF PARAMETERS FOR INTERACTION OF NONCONDENSIBLE WITH
CONDENSIBLE

DO 23 J = N1, NCOMP
IF (J-NR) 6, 23, 6
6 IF (J-NCRIT) 7, 7, 14
7 XLAMDA(K,J)=VLIQ(J)/VLIQ(K)
XLAMDA(J,K)=VLIQ(K)/VLIQ(J)
GO TO 23
14 IF (CACTCO(K,J,1)) 20, 16, 20
16 XLAMDA(K,J)=XLAMDA(K,NR)*HENRY(K,NR)/HENRY(K,J)
CACTCO(K,J,1) = -RT*ALOG(XLAMDA(K,J)*VLIQL(K,J)/VLIQ(J))
GO TO 22
20 XLAMDA(K,J) = (VLIQ(J)/VLIQL(K,J))*EXP(-CACTCO(K,J,1)/RT)
22 XLAMDA(J,K) = 0.0
23 CONTINUE

C

```

C      PARAMETERS FOR INTERACTION NON CONDENSIBLE PAIRS SET EQUAL TO
C      RATIO OF AVERAGE PARTIAL MOLAR VOLUMES AT INFINITE DILUTION
C
      DO 24 L = 1, NLIGHT
      XLAMDA(K,L)=VLIQ(L)/VLIQ(K)
24  CONTINUE
25  CONTINUE

C      CALCULATION OF PARAMETERS FOR INTERACTION OF COMPONENTS TREATED
C      IN THE SYMMETRIC CONVENTION.
C
30  DO 50 I = N1, NCOMP
      DO 40 J = N1, NCOMP
      IF((-CACTCO(I,J,1)/RT) .LT. -100.0) GO TO 35
      XLAMDA(I,J)=(VLIQ(J)/VLIQ(I))*EXP(-CACTCO(I,J,1)/RT)
      GO TO 40
35  XLAMDA(I,J) = 0.0
40  CONTINUE
50  CONTINUE

C      CALCULATION OF ACTIVITY COEFFICIENTS
C
55  DO 100 I = 1, NCOMP
      XLSUM = 0.0
      XSUM1 = 0.0
      DO 70 J = 1, NCOMP
C      XLSUM IS THE SUM IN THE LOGARITHMIC TERM
C
      XLSUM = XLSUM+X1(J)*XLAMDA(I,J)
      XSUM2 = 0.0
C
C      XSUM1 IS THE SUM OF THE NONLOG TERMS
C      XSUM2 IS THE SUM IN THE DENOMINATOR OF THE NON LOG TERMS
C
      DO 60 M = 1, NCOMP
      XSUM2 = XSUM2+X1(M)*XLAMDA(J,M)
60  CONTINUE
      XSUM1=XSUM1+X1(J)*XLAMDA(J,I)/XSUM2
70  CONTINUE
      XLSUM=XLSUM/SUMX
      IF (I-NLIGHT) 80, 80, 90
C
C      ACTIVITY COEFFICIENT OF NONCONDENSIBLE COMPONENTS REFERED TO
C      INFINITE DILUTION IN SPECIFIED REFERENCE SOLVENT , UNSYMMETRIC
C      CONVENTION.
C
80  NR = NRFFER(I)
      GAMMA(I) = (XLAMDA(I,NR)/XLSUM)/EXP(XSUM1)
      GO TO 100
C
C      ACTIVITY COEFFICIENT FOR CONDENSIBLE COMPONENTS, SYMMETRIC CONVENTION
C
90  GAMMA(I) = EXP(1.0-XSUM1)/XLSUM
100 CONTINUE
      RETURN
      END

```


SUBROUTINE PHIMIX (MARK)

C
C SUBROUTINE FOR CALCULATION OF VAPOUR PHASE FUGACITY COEFFICIENTS
C

0 DIMENSION TITLE(12), TCRIT(6,6), PCRT(6,6), VCRIT(6),
1 OMEGA(6), IDENT(6,2), VLIQ(6), CVLIQ(6,3), PSAT(6),
2 CPSAT(6,6), CACTCO(6,6,3), GAMMA(6), X(10,10), Y(10), PHI(6),
4 CHENRY(10,6,2), VLIQL(10,6), CVLIQL(10,6,2), OMEGAH(6),
3 B(6,6), F(6), FREFER(6), NREFER(6), HENRY(10,6)
DIMENSION DIPOLE(6), ETA(6), X1(10)
COMMON/SAI1/TITLE, NCOMP, NLIGHT, NACTCO, TCRIT, PCRT, VCRIT, OMEGA
COMMON/SAI2/IDENT, VLIQ, CVLIQ, PSAT, CPSAT, CACTCO, GAMMA, X, SUMX, Y
COMMON/SAI3/SUMY, P, T, TOLD, PHI, B, BMIX, VMIX, ZMIX, F, FREFER, NREFER
COMMON/SAI4/HENRY, CHENRY, VLIQL, CVLIQL, OMEGAH, DIPOLE, ETA, NCRIT, X1

C
C CALCULATE MOLAR VOLUME OF THE VAPOUR MIXTURE
C

PORT = P / (82.057 * T)
BMIX = 0.0
DO 15 I = 1, NCOMP
DO 10 J = 1, NCOMP
BMIX = BMIX + Y(I) * Y(J) * B(I,J)
10 CONTINUE
15 CONTINUE
BMIX = BMIX / SUMY ** 2
IF (MARK) 20, 20, 22
20 SQARG = 0.25 + BMIX * PORT

C
C IF BMIX TIMES P OVER R TIMES T IS MORE NEGATIVE THAN 0.25, THE
C PRESSURE SERIES VIRIAL EQUATION MUST BE USED. IN THIS CASE, THE
C ARGUMENT MARK IS USED TO COMMUNICATE THIS FACT TO THE MAIN PROGRAM
C

IF (SQARG) 22, 25, 25
22 VMIX = BMIX + 1. / PORT
ZMIX = PORT * VMIX
DO 24 I = 1, NCOMP
SUMB = 0.0
DO 23 J = 1, NCOMP
SUMB = SUMB + Y(J) * B(I,J)
23 CONTINUE
SUMB = SUMB / SUMY
PHI(I) = EXP((2.0 * SUMB - BMIX) * PORT)
24 CONTINUE
MARK = MARK + 1
RETURN
25 VMIX = (0.5 + SQRT(SQARG)) / PORT
ZMIX = PORT * VMIX

C
C CALCULATE FUGACITY COEFFICIENT OF EACH SPECIES
C

DO 40 I = 1, NCOMP
SUMB = 0.0
DO 30 J = 1, NCOMP
SUMB = SUMB + Y(J) * B(I,J)
30 CONTINUE
SUMB = SUMB / SUMY
PHI(I) = EXP(2.0 * SUMB / VMIX) / ZMIX
40 CONTINUE
RETURN
END

SUBROUTINE VIRIAL

C
C
C

SUBROUTINE FOR CALCULATION OF SECOND VIRIAL COEFFICIENTS

```

DIMENSION TITLE(12), TCRIT(6,6), PCRT(6,6), VCRIT(6),
1OMEGA(6), IDENT(6,2), VLIQ(6), CVLIQ(6,3), PSAT(6),
2CPSAT(6,6), CACTCO(6,6,3), GAMMA(6), X(10,10), Y(10), PHI(6),
4CHENRY(10,6,2), VLIQL(10,6), CVLIQL(10,6,2), OMEGAH(6),
3B(6,6), F(6), FREFER(6), NREFER(6), HENRY(10,6)
DIMENSION DIPOLE(6), ETA(6), X1(10)
COMMON/SAIL1/TITLE, NCOMP, NLIGHT, NACTCO, TCRIT, PCRT, VCRIT, OMEGA
COMMON/SAIL2/IDENT, VLIQ, CVLIQ, PSAT, CPSAT, CACTCO, GAMMA, X, SUMX, Y
COMMON/SAIL3/SUMY, P, T, TOLD, PHI, B, BMIX, VMIX, ZMIX, F, FREFER, NREFER
COMMON/SAIL4/HENRY, CHENRY, VLIQL, CVLIQL, OMEGAH, DIPOLE, ETA, NCRIT, X1
P2VPF(TR, RD) = -5.237220 + ALOG(RD) * (5.665807 + ALOG(RD) * (-2.133816
1+ ALOG(RD) * .2525373)) + (5.769770 + ALOG(RD) * (-6.181427 + ALOG(RD)
2* (2.283270 - ALOG(RD) * .2649074))) / TR
DO 202 I = 1, NCOMP
DO 201 J = 1, NCOMP
TR = T / TCRIT(I, J)
W = (OMEGA(I) + OMEGA(J)) / 2.0

```

C
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C

CALCULATE NONPOLAR SECOND VIRIAL COEFFICIENT FROM
CORRELATION OF PITZER AND CURL

```

0SEC VIR = (0.1445 + (0.330 + (0.1385 + 0.0121 / TR) / TR) / TR + W
1* (0.073 + (0.46 + (0.50 + (0.097 + 0.0073 / TR**5) / TR) / TR) / TR))

```

C
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C

ADD POLAR CONTRIBUTION AT REDUCED TEMPERATURE BELOW 0.95 WHEN
REDUCED DIPOLE MOMENT RD LARGER THAN 4.0

```

IF (DIPOLE(I) * DIPOLE(J)) 200, 200, 100
100 IF (0.95 - TR) 200, 200, 125
125 RD = 10.E04 * DIPOLE(I) * DIPOLE(J) * PCRT(I, J) / (TCRIT(I, J)**2)
IF (RD - 4.0) 200, 200, 135
135 SEC VIR = SEC VIR + P2VPF(TR, RD)

```

C
C

ADD CONTRIBUTION FOR MOLECULAR ASSOCIATION

```

150 IF (ETA(I) + ETA(J)) 200, 200, 175
175 SEC VIR = SEC VIR + 0.5 * (ETA(I) * ETA(J)) * EXP(6.6 * (0.7 - TR))
200 B(I, J) = SEC VIR * 82.057 * TCRIT(I, J) / PCRT(I, J)
B(J, I) = B(I, J)
201 CONTINUE
202 CONTINUE
RETURN
END

```

SUBROUTINE INPUT

SUBROUTINE TO READ IN ALL PURE COMPONENT DATA AND BINARY
INTER ACTION PARAMETERS

```

DIMENSION TITLE(12), TCRIT(6,6), PCRT(6,6), VCRIT(6),
1OMEGA(6), IDENT(6,2), VLIQ(6), CVLIQ(6,3), PSAT(6),
2CPSAT(6,6), CACTCO(6,6,3), GAMMA(6), X(10,10), Y(10), PHI(6),
4CHENRY(10,6,2), VLIQL(10,6), CVLIQL(10,6,2), OMEGAH(6),
3B(6,6), F(6), FREFER(6), NREFER(6), HENRY(10,6)
DIMENSION DIPOLE(6), ETA(6), X1(10)
COMMON/SAIL1/TITLE, NCOMP, NLIGHT, NACTCO, TCRIT, PCRT, VCRIT, OMEGA
COMMON/SAIL2/IDENT, VLIQ, CVLIQ, PSAT, CPSAT, CACTCO, GAMMA, X, SUMX, Y
COMMON/SAIL3/SUMY, P, T, TOLD, PHI, B, BMIX, VMIX, ZMIX, F, FREFER, NREFER
COMMON/SAIL4/HENRY, CHENRY, VLIQL, CVLIQL, OMEGAH, DIPOLF, ETA, NCRIT, X1
COMMON/FLEET/IFLG
IFLG=IFLG+1
READ(1,901)TITLE
READ(1,902)NCOMP, NLIGHT, NACTCO

```

NCOMP = TOTAL NO. OF COMPONENTS, NLIGHT = NO OF COMPONENTS TREATED
IN THE UNSYMMETRIC CONVENTION,
NACTCO = NO. OF BINARY INTERACTION PARAMETERS PER PAIR

NOTE - ARRANGE PURE COMPONENTS DATA IN ORDER OF INCREASING
CRITICAL TEMPERATURE

NACTCO = (NACTCO + 1) / 2
N1 = NLIGHT + 1
NCOMP1 = NCOMP - 1

READ IN PURE COMPONENT PROPERTIES - THREE CARDS FOR EACH SPECIES
1 - CRITICAL PROPERTIES / 2 - LIQUID VOLUMES / 3 - VAPOR PRESSURES
FOR SUPERCRITICAL COMPONENTS ONLY THE INFORMATION ON THE FIRST
CARD IS USED.

```

DO 90 I=1, NCOMP
10 READ (1,903) TCRIT(I,1), PCRT(I,1), VCRIT(I), OMEGA(I), OMEGAH(I),
11 DIPOLE(I), ETA(I), IDENT(I,1), IDENT(I,2)
IF(DIPOLE(I)) 33, 33, 36
33 OMEGAH(I) = OMEGA(I)
36 READ(1,904) T1, V1, T2, V2, T3, V3
READ(1,904) (CPSAT(I,J), J=1,6)
39 IF(T3) 40,40,70
40 CVLIQ(I,3) = 0.0
IF(T2) 50,50,60
50 CVLIQ(I,2) = 0.0
CVLIQ(I,1) = V1
GO TO 90
60 CVLIQ(I,2) = (V2-V1)/(T2-T1)
CVLIQ(I,1) = V1-CVLIQ(I,2)*T1
GO TO 90
70 CVLIQ(I,3) = ((T3 - T1) * (V2 - V1) - (V3 - V1) * (T2 - T1)) / ((T
12**2 - T1**2) * (T3 - T1) - (T3**2 - T1**2) * (T2 - T1))

```

```

      CVLIQ(I,2)=((V2-V1)-CVLIQ(I,3)*(T2**2-T1**2))/(T2-T1)
      CVLIQ(I,1)=V1-CVLIQ(I,2)*T1-CVLIQ(I,3)*T1**2
90  CONTINUE

C
C   CALCULATE CRITICAL PROPERTIES FOR BINARY INTERACTIONS
C
      DO 110 I=1,NCOMP1
      DO 100 J=I,NCOMP
        TCRIT(I,J)=SQRT(TCRIT(I,I)*TCRIT(J,J))
        PCRIT(I,J) = 4.0 * TCRIT(I,J) * (PCRIT(I,I) * VCRIT(I) / TCRIT(I,I)
        1) + PCRIT(J,J) * VCRIT(J) / TCRIT(J,J)) / (VCRIT(I)**0.3333333 +
        2 VCRIT(J)**0.3333333)**3
        TCRIT(J,I)=TCRIT(I,J)
        PCRIT(J,I)=PCRIT(I,J)
100  CONTINUE
110  CONTINUE
      IF (NLIGHT) 200, 200, 120

C
C   READ IN HENRY'S LAW CONSTANTS, PARTIAL MOLAR VOLUMES AT INFINITE
C   DILUTION, AND BINARY INTERACTION PARAMETERS.
C
120  DO 190 I=1,NLIGHT
      DO 180 J=N1,NCOMP
        READ(1,905) T1,H1,V1,T2,H2,V2, (CACTCO(I,J,K),CACTCO(J,I,K), K
        1 = 1, NACTCO)
        IF(CACTCO(I,J,1) + CACTCO(J,I,1)) 124,125,124
124  NREFER(I) = J
125  IF(V2) 130,130,140
130  CVLIQL(I,J,2)=(V2-V1)/(T2-T1)
      CVLIQL(I,J,1)=V1-CVLIQL(I,J,2)*T1
      GO TO 150
140  CVLIQL(I,J,2) = (V2-V1)/(T2-T1)
      CVLIQL(I,J,1) = V1-CVLIQL(I,J,2)*T1
150  IF(H2) 160,160,170
160  CHENRY(I,J,2)=0.0
      CHENRY(I,J,1)=H1
      GO TO 180
170  CHENRY(I,J,2) = ALOG(H1/H2)/ALOG(T1/T2)
      CHENRY(I,J,1)=H1/11**CHENRY(I,J,2)
180  CONTINUE
190  CONTINUE

C
C   READ IN BINARY INTERACTION PARAMETERS FOR COMPONENTS TREATED IN
C   THE SYMMETRIC CONVENTION,
C
      IF (N1 - NCOMP1) 200, 200, 240
200  DO 230 I = N1, NCOMP1
      I1=I+1
      DO 220 J = I1, NCOMP
        READ(1,905) (CACTCO(I,J,K),CACTCO(J,I,K),K=1,NACTCO)
220  CONTINUE
230  CONTINUE
240  TOLD = 0.0

C
C   SET ALL LIKE-PAIR INTERACTION COEFFICIENTS EQUAL TO ZERO
C
      DO 260 J = 1, NCOMP
      DO 250 K = 1, NACTCO
        CACTCO(J,J,K) = 0.0
250  CONTINUE
260  CONTINUE
901  FORMAT (12A6)
902  FORMAT (314)
903  FORMAT (7F8.4,2A6)
904  FORMAT(6F0.0)
905  FORMAT(8F0.0)
906  FORMAT(6I0)
      RETURN
      END

```

SUBROUTINE OUTPUT

C
C
C

SUBROUTINE FOR PRINTING PHASE EQUILIBRIUM RESULTS

```

0DIMENSION TITLE(12), TCRIT(6,6), PCRT(6,6), VCRIT(6),
1OMEGA(6), IDENT(6,2), VLIQ(6), CVLIQ(6,3), PSAT(6),
2CPSAT(6,6), CACTCO(6,6,3), GAMMA(6), X(10,10), Y(10), PHI(6),
4CHENRY(10,6,2), VLIQL(10,6), CVLIQL(10,6,2), OMEGAH(6),
3B(6,6), F(6), FREFER(6), NREFER(6), HENRY(10,6)
  DIMENSION DIPOLE(6), ETA(6), X1(10)
  COMMON/SAI1/TITLE, NCOMP, NLIGHT, NACTCO, TCRIT, PCRT, VCRIT, OMEGA
  COMMON/SAI2/IDENT, VLIQ, CVLIQ, PSAT, CPSAT, CACTCO, GAMMA, X, SUMX, Y
  COMMON/SAI3/SUMY, P, T, TOLD, PHI, B, BMIX, VMIX, ZMIX, F, FREFER, NREFER
  COMMON/SAI4/HENRY, CHENRY, VLIQL, CVLIQL, OMEGAH, DIPOLE, ETA, NCRIT, X1
  WRITE(2,920)TITLE
  WRITE(2,921)T,P
  WRITE(2,922)VMIX,BMIX
  IF(NLIGHT)303,303,301
301 WRITE(2,923)
C
C
C   PRINT RESULTS FOR COMPONENTS TREATED IN THE UNSYMETRIC CONVENTION
C
  DO 304 I=1,NLIGHT
  NR=NREFER(I)
  WRITE(2,924) IDENT(I,1),IDENT(I,2),X1(I),Y(I),F(I),GAMMA(I),
1PHI(I),IDENT(NR,1),IDENT(NR,2),HENRY(I,NR),VLIQL(I,NR)
302 CONTINUE
303 N1=NLIGHT+1
  WRITE(2,925)
C
C
C   PRINT RESULTS FOR COMPONENTS TREATED IN THE SYMMETRIC CONVENTION
C
  WRITE(2,926)(IDENT(I,1),IDENT(I,2),X1(I),Y(I),F(I),GAMMA(I),
1PHI(I),PSAT(I),VLIQ(I),I=N1,NCOMP)
920 FORMAT(1H1,13X,12A6,////)
921 FORMAT( 2X,14HTEMPERATURE = ,F8.3, 15H DEGREES KELVIN, 23X, 20H
2TOTAL PRESSURE = ,F9.5, 12H ATMOSPHERES )
922 FORMAT(23H0 VAPOR MOLAR VOLUME = ,F8.2, 12H CC./G.=MOLE, 6X, 33H
1MIXTURE SECOND VIRIAL COEFF. = ,F8.1, 12H CC./G.=MOLE, ///)
923 FORMAT(100HUNSYMMETRIC CONVENTION      X      Y      FUGACITY      G
1AMMA      PHI      REF COMP HENRY C. VOL.(ID), //)
924 FORMAT(10X, 2A4, 2X, 5F10.4, 2X, 2A4, F10.4, F10.2)
925 FORMAT (///, 100HSYMMETRIC CONVENTION      X      Y      FUGACIT
1Y      GAMMA      PHI      VAPOR PRESSURE      LIQUID VOL., //)
926 FORMAT(10X, 2A4, 2X, 5F10.4, F12.4, F14.2)
  RETURN
  END

```



```

SUBROUTINE MODCON(Y,P,T)
C
C SUBROUTINE FOR CALCULATION OF VAPOUR PHASE
C MOLE FRACTIONS AT CHEMICAL EQUILIBRIA
C
C DIMENSION Y(20)
C
C FUNCTION STATEMENTS
C TEMPERATURE DEPENDENCE OF
C EQUILIBRIUM CONSTANTS OF REACTIONS
C
C CK1(T) = 10.0**(9.8-3200.0/T)
C CK2(T) = 10.0**(8.2-3200.0/T)
C F1 = CK1(T)
C F2 = CK2(T)
C
C COEFFICIENTS OF CUBIC EQUATION DEFINING ALFA
C
C A = P*F2+F1*F2-P*F1-F1**2
C B = P*F2*Y(2)+2.0*F1*F2*Y(2)+P*F1*Y(3)+2.0*P*F2*Y(5)+2.0*F1*F2*Y(
15)+P*F2*Y(1)+F1*F2*Y(1)+F1*F2*Y(3)-P*F1*Y(5)-P*F1*Y(1)-F1**2*Y(1)
2=F1**2*Y(5)-F1**2*Y(2)+P*F1*Y(4)+F1**2*Y(4)
C C = 2.0*P*F2*Y(5)*Y(2)+2.0*F1*F2*Y(5)*Y(2)-2.0*F1*F2*Y(4)*Y(2)
1=P*F1*Y(3)*Y(4)+P*F1*Y(3)*Y(5)+P*F2*Y(5)**2+2.0*P*F2*Y(5)*Y(1)
2*F1*F2*Y(5)*Y(1)-2.0*F1*F2*Y(5)*Y(4)+F1*F2*Y(5)**2*F1*F2*Y(5)*Y(4)
3*F1*F2*Y(3)*Y(5)-F1*F2*Y(1)*Y(4)-F1*F2*Y(4)**2-F1*F2*Y(3)*Y(4)
4=P*F1*Y(5)*Y(1)+F1**2*Y(1)*Y(4)+2.0*F1**2*Y(5)*Y(4)
5*2.0*F1**2*Y(2)*Y(4)+P*F1*Y(5)*Y(4)+P*F1*Y(1)*Y(4)+F1**2*Y(4)**2
6*F1**2*Y(1)*Y(4)
C D = P*F2*Y(5)**2*Y(1)+P*F2*Y(5)**2*Y(2)-F1*F2*Y(5)*Y(4)*Y(2)
1=P*F1*Y(5)*Y(3)*Y(4)-F1*F2*Y(1)*Y(4)*Y(5)-F1*F2*Y(5)**2*Y(4)
2=F1*F2*Y(5)*Y(4)**2-F1*F2*Y(3)*Y(4)*Y(5)-F1*F2*Y(2)*Y(4)*Y(5)
3+P*F1*Y(5)*Y(4)*Y(1)-F1**2*Y(1)*Y(4)**2-F1**2*Y(5)*Y(4)**2
4=F1**2*Y(4)**3-F1**2*Y(4)**2*Y(2)
C
C NEWTON RAPHSON METHOD FOR SOLUTION OF CUBIC EQUATION
C
C X=0.0
C I = 0
10 FUN = A*X**3+B*X**2+C*X+D
DFUN = 3.0*A*X**2+2.0*B*X+C
X1 = X-FUN/DFUN
IF (ABS(X-X1).LT.0.000001) GO TO 20
IF (1.GT.300) GO TO 30
X = X1
I = I+1
GO TO 10
30 WRITE(2,40)
40 FORMAT(10X,15H NO CONVERGENCE ,/)
STOP
20 ALF = X1
BET = (-F2*Y(5)*Y(2)-ALF*F2*Y(2)+F1*Y(3)*Y(4)-ALF*F1*Y(3))/(-F2*
1Y(5)-ALF*F2+ALF*F1-F1*Y(4))
S = Y(1)+Y(2)+Y(3)+Y(4)+Y(5)+ALF+BET
C
C VAPOUR PHASE MOLE FRACTIONS AT CHEMICAL EQUILIBRIA
C
C Y(1) = (Y(1)+ALF+BET)/S
C Y(2) = (Y(2)+BET)/S
C Y(3) = (Y(3)+BET)/S
C Y(4) = (Y(4)+ALF)/S
C Y(5) = (Y(5)+ALF)/S
C RETURN
C END

```



```

SUBROUTINE BUBLDILF(XK, YK, TK, PK)
C
C THIS VERSION OF THE SUBROUTINE IS USED ONLY FOR
C PHASE EQUILIBRIUM CALCULATIONS
C
C MAIN PROGRAM FOR CALCULATION OF TEMPERATURE AND VAPOUR COMPOSITION
C FROM LIQUID COMPOSITION AND TOTAL PRESSURE DATA
C
C VAPOUR LIQUID EQUILIBRIA WITH CHEMICAL REACTION IN LIQUID AND
C VAPOUR PHASES
C
  DIMENSION YK(5), XK(5), CL(5)
  DIMENSION TITLE(12), YCRIT(6,6), PCRIT(6,6), VCRIT(6),
  1 OMEGA(6), IDENT(6,2), VLIQ(6), CVLIQ(6,3), PSAT(6),
  2 CPSAT(6,6), CACTCO(6,6,3), GAMMA(6), X(10,10), Y(10), PHI(6),
  4 CHENRY(10,6,2), VLIQL(10,6), CVLIQL(10,6,2), OMEGAH(6),
  3B(6,6), F(6), FREFER(6), NREFER(6), HENRY(10,6)
  DIMENSION DIPOLE(6), ETA(6), X1(10)
  COMMON/SAI1/TITLE, NCOMP, NLIGHT, NACTCO, TCRIT, PCRIT, VCRIT, OMEGA
  COMMON/SAI2/IDENT, VLIQ, CVLIQ, PSAT, CPSAT, CACTCO, GAMMA, X, SUMX, Y
  COMMON/SAI3/SUMY, P, T, TOLD, PHI, B, BMIX, VMIX, ZMIX, F, FREFER, NREFER
  COMMON/SAI4/HENRY, CHENRY, VLIQL, CVLIQL, OMEGAH, DIPOLE, ETA, NCRIT, X1
  COMMON/FLEET/IFLG
  P = PK
  T = TK
  SUMX = 1.0
  IF(IFLG, NE, 0) GO TO 509
500 CALL INPUT
509 CONTINUE
  DO 12 I=1, NCOMP
    X1(I) = XK(I)
  12 CONTINUE
  DO 510 I=1, NCOMP
    PHI(I) = 1.0
  510 CONTINUE
  IF(P) 660, 500, 530
530 TPREV = 0.0
  WRITE(2,1002) TITLE
  WRITE(2,1000)
C
C BEGIN A TEMPERATURE ITERATION
C
540 RT=82.057 * T
  KOUNT = 0
  CALL VIRIAL
  CALL RSTATE

```

```

CALL ACTCO
TOLD = T
SUMY = 0.0
DO 550 I=1,NCOMP
F(I) = X1(I) * GAMMA(I) * FREFER(I) * EXP(VLIQ(I) * P / RT)
Y(I) = F(I) / (P*PHI(I))
SUMY = SUMY + Y(I)
YM(I) = Y(I)
550 CONTINUE
CALL MODCON(YM,P,T)
SUMY = 0.0
DO 551 I=1,NCOMP
Y(I) = YM(I)
SUMY = SUMY+Y(I)
551 CONTINUE
PINT = 0.0
DO 555 I=1,NCOMP
PINT = PINT+F(I)/PHI(I)
555 CONTINUE
PINTO = PINT
MARK = -1

C
C BEGIN AN ITERATION TO FIND VAPOUR PHASE FUGACITY COEFFICIENTS
C
560 CALL PHIMIX(MARK)
IF(VMIX) 650, 650, 565
565 KOUNT = KOUNT +1
SUMY = 0.0
DO 570 I=1,NCOMP
Y(I) = F(I) / (P*PHI(I))
SUMY = SUMY + Y(I)
YM(I) = Y(I)
570 CONTINUE
CALL MODCON(YM,P,T)
SUMY = 0.0
DO 571 I=1,NCOMP
Y(I) = YM(I)
SUMY = SUMY+Y(I)
571 CONTINUE
PINT = 0.0
DO 575 I=1,NCOMP
PINT = PINT + F(I)/PHI(I)
575 CONTINUE

C
C CHECK TO SEE WHETHER PRESSURE IS CONSTANT
C
IF(ABS(PINT-PINTO)/PINT-1,0E-4) 590, 590, 580
580 PINTO = PINT
GO TO 560

C
C CHECK FOR THE CONVERGENCE OF CALCULATED PRESSURE
C TO ACTUAL PRESSURE
C
590 SUMY1 = PINT * P
WRITE(2,1001)T,SUMY,KOUNT,(I,X1(I),Y(I),F(I),FREFER(I)
1, GAMMA(I), VLIQ(I), R(I,I), PHI(I)), I=1,NCOMP)
IF (ABS(SUMY1)-1,0E-4) 650, 650, 595
595 IF (TPREV) 600, 600, 615
600 PINTP = PINT
TPREV = T
IF (SUMY1) 605, 650, 610
605 T = T * 1.020
GO TO 540
610 T = T * 0.980
GO TO 540
C

```

```

C      ADJUST THE TEMPERATURE AND START ANOTHER ITERATION
C
615  SLOPE = (T-TPREV)/(PINT-PINTP)
      PINTP = PINT
      TPREV = T
      DELT = SLOPE*SUNY1
      IF (ABS (DELT) - 0.1 * T) 625, 625, 620
620  DELT = SIGN(0.1 * T, DELT)
625  T = T - DELT
      GO TO 540
650  CALL OUTPUT
      IF (MARK) 660, 655, 655
655  WRITE(2,923)
C
C      ADJUSTMENT OF VAPOUR COMPOSITION AND TEMPERATURE
C      FOR SOLUTIONS WITH METHANOL CONTENT OF 0.01 TO 0.12
C
660  IF (X1(3) GE 0.12 OR X1(3) LT 0.01) GO TO 700
      XDM1 = (X1(1)+X1(2)+X1(4))/(1.0+X1(2)+X1(4))
      XDM3 = (X1(2)+X1(3))/(1.0+X1(2)+X1(4))
      XDM5 = (X1(4)+X1(5))/(1.0+X1(2)+X1(4))
      YDM1 = (Y(1)+Y(2)+Y(4))/(1.0+Y(2)+Y(4))
      YDM3 = (Y(2)+Y(3))/(1.0+Y(2)+Y(4))
      YDM5 = (Y(4)+Y(5))/(1.0+Y(2)+Y(4))
      T = T+3.0
      YM(1) = YDM1+0.144931*XDM1**0.341386+0.943512*XDM2**
11.50803+0.016604
      YM(2) = 0.0
      YM(3) = YDM3+0.514208*XDM1**0.797498+0.905221*XDM3**
10.034031+0.18591*XDM5**5+0.953265
      YM(4) = 0.0
      YM(5) = YDM5+0.222355*XDM1**0.176251+0.839034*XDM3**
1(-0.0211675)+0.0931838*XDM5**2.28577-1.10191
      CALL MODCON(YM, P, T)
      DO 670 I=1,NCOMP
        Y(I) = YM(I)
670  CONTINUE
700  DO 710 I=1,NCOMP
        YK(I) = Y(I)
        XK(I) = X1(I)
710  CONTINUE
      TK = T
      RETURN
923  FORMAT(///,102H VOLUME SERIES VIRIAL EQUATION HAS IMAGINARY SOLUTI
1ONS -- PRESSURE SERIES USED FOR FINAL CALCULATIONS )
10000FORMAT(120H0      TEMP.      SUMY      LAPS      COMP.      X
1  Y      F      FREFER      GAMMA      VL,Q      B      PH1 ,
2 // )
10010FORMAT(1H0,7X, F10.4, F10.6, 14, 18, 5F10.4, 2F10.2, F10.4, /(
134X, 16, 5F10.4, 2F10.2, F10.4))
10020FORMAT(1H1, 23X, 12A6, 18X, 8HBUBLDILF , //)
      END

```

```
MASTER SD
C
C   MAIN SEGMENT FOR VAPOUR LIQUID EQUILIBRIUM ACCOMPANIED
C   WITH A CHEMICAL REACTION
C
C   THIS PROGRAM REQUIRES THE FOLLOWING SUBROUTINES
C   BURLDILF, INPUT, RSTATE, PHIMIX, ACTCO, VIRIAL, OUTPUT
C   AND MODCON
C
C   DIMENSION X(5), Y(5), Z1(20), Z2(20), Z3(20), Z4(20)
C   COMMON/FLEET/IFLG
C
C   READ NO. OF DATA POINTS, INITIAL GUESS FOR TEMPERATURE
C   AND LIQUID PHASE MOLE FRACTIONS
C
C   READ(1,120) N, TEMP
C   DO 100 I=1,N
C   READ(1,130) Z1(I), Z2(I), Z3(I), Z4(I)
100  CONTINUE
C   READ(1,130)P
C   IFLG = 0
C   T = TEMP
C   DO 110 I=1,N
C   X(1) = Z1(I)
C   X(2) = Z2(I)
C   X(3) = Z3(I)
C   X(4) = Z4(I)
C   X(5) = 1.0-Z1(I)-Z2(I)-Z3(I)-Z4(I)
C
C   START OF PHASE EQUILIBRIUM CALCULATIONS
C
C   CALL BURLDILF(X, Y, T, P)
110  CONTINUE
120  FORMAT(10,F),0)
130  FORMAT(4F0.0)
C   STOP
C   END
```


APPENDIX VII

COMPUTER PROGRAMS FOR PARAMETER ESTIMATION

Listing of programs for estimation of various parameters are given in this Appendix. The listing includes the following segments;

1. Program VAPFIT
2. Subroutine BMARQ
3. Subroutine BSOLVE
4. Subroutine EVALU
5. Subroutine CALPLW
6. Program COMP5


```

MASTER VAPFIT
C
C PROGRAM TO OBTAIN PARAMETERS OF FOUR PARAMETER VAP. PRES. EQN.
C
  DIMENSION TID(12), IDENT(2), T(20), P(20), CPSAT(10),
1 PCTERR(20), PCAL(20), DEL(20), PCBEST(20), DLBEST(20)
  CALL UAMILLTIME(START)
  LAPMAX = 100
  DCPMIN=0.00001
C
C READ IN AN IDENTIFICATION CARD FOR THE SUBSTANCE
C
  1 READ(1,2) TID
  2 FORMAT(12A6)
C
C N=NO. DATA POINTS , TCRIT =CRITICAL TEMPRATURE,
C PCRIT = CRITICAL PRESSURE, WEIGHT = MOLECULAR WEIGHT,
C TFIX IS AN ADDITIVE CONSTANT TO CONVERT INPUT PRESSURE TO ATMOSPHERE
C PFIX IS A DIVISER TO CONVERT INPUT TEMP TO DEG. KELVIN
C ERRMAX IS DESIRABLE PER CENT ERROR IN PRESSURE.
C IDENT IS AN EIGHT CHARACTER IDENTIFICATION FOR THE SUBSTANCE.
C TCRIT IN DEGREES KELVIN AND PCRIT IN ATMOSPHERES
C ALL OTHER TEMPERATURE AND PRESSURES OF INPUT IN UNITS SUCH THAT
C TFIX AND PFIX CORRECT THEM TO DEGREES KELVIN AND ATMOSPHERES.
C
  READ (1,10)N,TCRIT,PCRIT,WEIGHT,TFIX,PFIX,ERRMAX,IDENT
10  FORMAT(18, 6F8.4, 16X, 2A4)
  IF(N)999,999,11
11  POINTS=N
  STOPSQ=POINTS*ERRMAX**2
C
C READ THREE TEMPERATURE AND DENSITY SETS. DENSITY IN GM/CC
C
  READ(1,20)T1, D1, T2, D2, T3, D3
20  FORMAT(6F12.6)
  V1=WEIGHT/D1
  V2=WEIGHT/D2
  V3=WEIGHT/D3
  T1=T1+TFIX
  T2=T2+TFIX
  T3=T3+TFIX
C
C READ TEMPERATURE AND PRESSURE SETS
C
  DO 30 I=1,N
C
C NORMALIZE TEMPERATURE TO (DEGREES KELVIN) /100 TEMPERATURE SCALE
C
  READ(1,20)T(I),P(I)

```

```

T(I)=(T(I)+TFIX)/100.
P(I)=P(I)/PFIX
30  CONTINUE
    LAP=0

C
C  CALCULATION OF MATRIX COMPONENTS AND MATRIX INVERSION
C  FOR LEAST SQUARES FITTING OF INPUT DATA
C
    TSUM=0.0
    T2SUM=0.0
    T3SUM=0.0
    T4SUM=0.0
    DO 40 J=1,N
        TSUM=TSUM+T(J)
        T2SUM=T2SUM+T(J)**2
        T3SUM=T3SUM+T(J)**3
        T4SUM=T4SUM+T(J)**4
40  CONTINUE
    CPSAT(6)=0.0
    DCPSAT=-10.0
    SQBEST=1.0E+30
    SUMSQ=1.0E+30
52  LAP=LAP+1
    PSUM=0.0
    PTSUM=0.0
    PT2SUM=0.0
    DO 55 J=1,N
        PT=(ALOG(P(J))-CPSAT(6)*ALOG(T(J)))*T(J)
        PSUM=PSUM+PT
        PTSUM=PTSUM+PT*T(J)
        PT2SUM=PT2SUM+PT*T(J)**2
55  CONTINUE
    Z1=PSUM*T3SUM-PTSUM*T2SUM
    Z2=PTSUM*T4SUM-PT2SUM*T3SUM
    A11=POINTS*T3SUM-TSUM*T2SUM
    A12=TSUM*T3SUM-T2SUM*T2SUM
    A21=TSUM*T4SUM-T2SUM*T3SUM
    A22=T2SUM*T4SUM-T3SUM*T3SUM
    CPSAT(2)=(A22*Z1-Z2*A12)/(A11*A22-A12*A21)
    CPSAT(1)=(Z1-A11*CPSAT(2))/A12
    CPSAT3=0.0
    CPSAT(4)=(PSUM-POINTS*CPSAT(2)-TSUM*CPSAT(1))/T2SUM
    CPSAT(5)=0.0

C
C  COMPUTE SUM SQUARE ERROR
C
    SUMSQ=0.0
    DO 75 I=1,N
        PCAL(I)=EXP(CPSAT(1)+CPSAT(2)/T(I)+CPSAT(4)*T(I)
1 + CPSAT(6)*ALOG(T(I)))
        DEL(I)=P(I)-PCAL(I)
        PCTERR(I)=ABS(100.0*DEL(I)/P(I))
        SUMSQ=SUMSQ+PCTERR(I)**2
75  CONTINUE

C
C  CHECKS FOR PROGRAM TERMINATION
C
    IF(LAP-1)121,121,119
119 IF(LAP-LAPMAX)120,500,500
120 IF(SUMSQ-SQBEST)121,125,125
121 SQBEST=SUMSQ
    LPBEST=LAP

C
C  SAVE RESULTS OF BEST PARAMETER SET
C
    DO 124 I=1,N

```

```

PCBEST(1)=PCAL(1)
DLBEST(1)=DEL(1)
122 CONTINUE
C1BEST=CPSAT(1)-CPSAT(6)*ALOG(100.)
C2BEST=CPSAT(2)*100.
C3BEST=CPSAT(3)
C4BEST=CPSAT(4)/100.
C5BEST=CPSAT(5)/10000.
C6BEST=CPSAT(6)
IF(SQBEST-STOPSQ)500,500,130
125 IF(SUMSQ-SUMSQP)130,130,126
C
C INCREMENT CPSAT(6), RECOMPUTE AND INVERT MATRICES UNTIL
C BEST FIT IS OBTAINED
C
126 DCPSAT=-DCPSAT/10.0
IF(ABS(DCPSAT)-DCPMIN)500,500,130
130 CPSAT(6)=CPSAT(6)+DCPSAT
SUMSQP=SUMSQ
GO TO 52
500 CONTINUE
RMSERR=SQRT(SQBEST/POINTS)
WRITE(2,520) TID
520 FORMAT(1H1, 12A6, '/')
WRITE(2,530)C1BEST, C2BEST, C3BEST, C4BEST, C5BEST, C6BEST
5300 FORMAT(46H PARAMETERS FOR THE SATURATION PRESSURE CURVE //,
164H LN(PCAL) = C(1) + C(2)/C(3)+T + C(4)*T + C(5)*T**2 + C(6)*LN(T
2)//,12H CPSAT(1) = , F14.6/ 12H CPSAT(2) = , F14.6/ 12H CPSAT(3) =
3 , F14.6/ 12H CPSAT(4) = ,4X, E14.6/ 12H CPSAT(5) = , 4X,
4 E14.6/ 12H CPSAT(6) = , F14.6//)
WRITE(2,560)
5600 FORMAT(1H0, 8X,53HTEMPERATURE PEXP PCALC DELTA PCT.
1ERR. , //)
SUM=0.0
AVGPCT=0.0
DO 580 I=1,N
T(I)=T(I)*100.0
WRITE(2,570)T(I),P(I),PCBEST(1),DLBEST(1),PCTERR(1)
570 FORMAT(10X, F10.3, 3F10.5, F10.3)
SUM=SUM+ABS(DLBEST(I))
AVGPCT=AVGPCT+PCTERR(I)
580 CONTINUE
AVDMAG=SUM/POINTS
AVGPCT=AVGPCT/POINTS
WRITE(2,590)AVDMAG
5900 FORMAT(1H0, 5X, 44HMEAN ABSOLUTE MAGNITUDE OF THE DEVIATIONS = ,
1 F8.5)
WRITE(2,591)AVGPCT
591 FORMAT(6X, 38HMEAN ABSOLUTE PERCENTAGE DEVIATION = , F12.3)
TR7=0.7*TCRIT
PR7=EXP(C1BEST+C2BEST/TR7+C4BEST*TR7
1+ C6BEST*ALOG(TR7))/PCRIT
OMEGA=-1.0-0.43429448*ALOG(PR7)
VCRIT=(0.291-0.08*OMEGA)*TCRIT*82.057/PCRIT
WRITE(2,600)TCRIT, PCRIT, VCRIT, OMEGA
6000 FORMAT(9H0TCRIT = , F8.3, 2X, 9H PCRIT = , F8.3, 2X, 9H VCRIT =
1, F8.3, 2X, 9H OMEGA = , F8.4)
WRITE(2,608)T1,V1,T2,V2,T3,V3
608 FORMAT(9H0TEMP1 = , F8.3, 2X, 9H VOL 1 = , F8.3, 2X, 9H TEMP2 = ,
1F8.3, 2X, 9H VOL 2 = , F8.3, 2X, 9H TEMP3 = , F8.3, 2X, 9H VOL 3 =
2 , F8.3 //)
CALL UAMILLTIME(END)
THETA =END -START
START=END
WRITE(2,525)SQBEST, LPBEST, RMSERR, LAP, THETA
5250 FORMAT(37H0SUM OF SQUARES OF PCT. DEVIATION = , F8.4, 6X, 11HBEST
1 LAP = , I3, / 37H ROOT MEAN SQUARE PERCENT DEVIATION = , F8.4,
26X, 11HLAST LAP = , I3, 4X, 7HTIME = , F5.2)
GO TO 1
999 CALL EXIT
END
FINISH

```

```

SUBROUTINE BMARQ(B1, KK1, NN1, Y2, PH1)
C
C
C   MAIN PROGRAM FOR MINIMIZATION OF THE OBJECTIVE FUNCTION
C
  DIMENSION P(100), A(20,20), AC(20,20), B(10), Z(20), V(20),
1 BV(20), BMIN(10), BMAX(10), DV(20)
  DIMENSION Y2(20), B1(30)
  COMMON /DECK/ KK, B, NN, Z, Y, PH, FNU, FLA, TAU, EPS, PHMIN, I, ICON, FV, DV
  COMMON /HAUL/ BV, BMIN, BMAX, P, FUNC, DERIV, KD, A, AC, GAMM
  NN = NN1
  KK = KK1
  DO 42 I=1, NN
  Y(I) = Y2(I)
42  CONTINUE
  DO 43 I=1, KK
  B(I) = B1(I)
43  CONTINUE
C
C   SET THE LIMITS ON THE VARIABLES
C
  DO 12 J=1, KK
  BMIN(J) = -100000.
  BMAX(J) = 1000000.0
12  CONTINUE
C
C   INITIALIZE THE PROGRAM VARIABLES
C
  FNU=0.0
  FLA=0.0
  TAU=0.0
  EPS=0.0
  PHMIN=0.0
  I=0
  KD=KK
  FV=0.0
  DO 100 J=1, KK
  BV(J)=1.
100  CONTINUE
  ICON = KK
  ITER = 0
C
C   START OPTIMIZATION CALCULATIONS
C
200  CALL BSOLVE
C
  ITER=ITER+1
C
C   PRINT STATEMENTS

```


C

```
      WRITE(2,1) ICON, PH, IYER
1     FORMAT(/,2X,6HICON = ,I3,4X, 5HPH = ,E15.8,4X, 16HITERATION NO. =
      ,I3 )
      IF (ICON) 10,300,200
10    IF (ICON+1) 20,60,200
20    IF (ICON+2) 30,70,200
30    IF (ICON+3) 40,80,200
40    IF (ICON+4) 50,90,200
50    GO TO 95
60    WRITE(2,4)
      4    FORMAT (//,2X,32HNO FUNCTION IMPROVEMENT POSSIBLE )
      GO TO 300
70    WRITE (2,5)
      5    FORMAT (//,2X, 28HMORE UNKNOWNNS THAN FUNCTIONS )
      GO TO 300
80    WRITE (2,6)
      6    FORMAT (//,2X, 24HTOTAL VARIABLES ARE ZERO )
      GO TO 300
90    WRITE (2,7)
      7    FORMAT (//,2X,80HCORRECTIONS SATISFY CONVERGENCE REQUIRMENTS BUT
1     LAMDA FACTOR (FLA) STILL LARGE )
      GO TO 300
95    WRITE (2,8)
      8    FORMAT(//,2X, 20HTHIS IS NOT POSSIBLE )
      GO TO 300
300   WRITE (2,2)
      2    FORMAT (//,2X, 26HSOLUTIONS OF THE EQUATIONS )
      DO 400 J=1,KK
      WRITE(2,3) J, B(J)
      3    FORMAT (/,2X, 2HB(,I2,4H) = ,E16.8 )
      B1(I) = B(I)
400   CONTINUE
1000  CONTINUE
      PH1 = PH
      RETURN
      END
```



```

SUBROUTINE BSOLVE
C
C   MAIN SUBROUTINE FOR OPTIMIZATION CALCULATIONS
C
  DIMENSION P(100),A(20,20),AC(20,20),B(10),Z(20),Y(20),
1BV(20), BMIN(10), BMAX(10), FV(20), DV(20)
  DIMENSION TRAN1(30), TRAN2(20)
  COMMON /DECK/KK,B,NN,Z,Y,PH,FNU,FLA,TAU,EPS,PHMIN,I,ICON,FV,DV
  COMMON /HAUL/ BV,BMIN,BMAX,P,FUNC,DERIV,KD,A,AC,GAMM
C
  K= KK
  N= NN
  KP1 = K+1
  KP2 = KP1+1
  KBI1 = K*N
  KBI2 = KBI1+K
  KZI = KBI2 + K
  DO 101 J6=1,K
    BV(J6)=1.0
101  CONTINUE
    IF ( FNU .LE. 0. ) FNU = 10.0
    IF ( FLA .LE. 0. ) FLA = 0.01
    IF ( TAU .LE. 0. ) TAU = 0.001
    IF ( EPS .LE. 0. ) EPS = 0.00002
    IF ( PHMIN .LE. 0. ) PHMIN = 0.
120  KE= 0
130  DO 160 I1 =1,K
160  IF ( BV(I1) .NE. 0. ) KE = KE+ 1
    IF ( KE .GT. 0 ) GO TO 170
162  ICON = -3
163  GO TO 2120
170  IF ( N .GE. KE ) GO TO 500
180  ICON = -2
190  GO TO 2120
500  I1 = 1
530  IF ( I .GT. 0 ) GO TO 1530
550  DO 560 J1 = 1,K
    J2 = KBI1 + J1
    P(J2)= B(J1)
    J3 = KBI2 + J1
560  P(J3) = ABS(B(J1)) + 1.0E+02
    GO TO 1030
590  IF ( PHMIN .GT. PH .AND. I .GT. 1 ) GO TO 625
    DO 620 J1= 1,K
    N1= (J1 - 1)*N
    IF ( BV(J1) ) 601, 620, 605
601  BV(J1) = 1.0
605  DO 606 J2= 1,K
    J3 = KBI1 + J2
606  P(J3)= B(J2)

```

```

J3 = KBI1 + J1
J4 = KBI2 + J1
DEN = 0.001*AMAX1(P(J4),ABS(P(J3)))
IF (P(J3) + DEN .LE. BMAX(J1)) GO TO 55
P(J3) = P(J3) - DEN
DEN = -DEN
GO TO 56
55 P(J3) = P(J3) + DEN
56 DO 57 IJ=1,K
   TRAN1(IJ)= P(KBI1+IJ)
57 CONTINUE
   CALL EVALU(K,TRAN1,N,TRAN2,FV)
   DO 58 IJ=1,N
     P(N1+IJ)= TRAN2(IJ)
58 CONTINUE
   DO 610 J2 =1,N
     JB = J2 + N1
610 P(JB) = (P(JB) - Z(J2))/DEN
620 CONTINUE
C
C   SET UP CORRECTION EQUATIONS
C
625 DO 725 J1 =1,K
     N1 = (J1 - 1)*N
     A(J1,KP1) = 0.
     IF ( BV(J1) ) 630, 692, 630
630 DO 640 J2 =1,N
     N2 = N1 + J2
640 A(J1,KP1) = A(J1,KP1) + P(N2)*(Y(J2) - Z(J2))
650 DO 680 J2 =1,K
660 A(J1,J2) = 0.
665 N2 = (J2-1)*N
670 DO 680 J3=1,N
672 N3 = N1 + J3
674 N4 = N2 + J3
680 A(J1,J2) = A(J1,J2) + P(N3)*P(N4)
     IF ( A(J1,J1) .GT. 1.E=20) GO TO 725
692 DO 694 J2=1,KP1
694 A(J1,J2) = 0.
695 A(J1,J1) = 1.0
725 CONTINUE
     GN = 0.
     DO 729 J1 =1,K
729 GN = GN + A(J1,KP1)**2
C
C   SCALE CORRECTION EQUATIONS
C
DO 726 J1 =1,K
726 A(J1,KP2) = SQRT(A(J1,J1))
     DO 727 J1 =1,K
       A(J1,KP1) = A(J1,KP1)/A(J1,KP2)
     DO 727 J2 =1,K
       A(J1,J2) = A(J1,J2)/(A(J1,KP2)*A(J2,KP2))
727 A(J1,J2) = A(J1,J2)/(A(J1,KP2)*A(J2,KP2))
730 FL = FLA/FNU
     GO TO 810
800 FL = FNU*FL
810 DO 840 J1 =1,K
820 DO 830 J2 =1,KP1
830 AC(J1,J2) = A(J1,J2)
840 AC(J1,J1)= AC(J1,J1) + FL
C
C   SOLVE CORRECTION EQUATIONS
C
DO 930 L1 =1,K
L2 = L1 + 1

```

```

DO 910 L3=L2,KP1
910 AC(L1,L3) = AC(L1,L3)/AC(L1,L1)
DO 930 L3 = 1,K
IF ( L1=L3) 920, 930, 920
920 DO 925 L4 = L2,KP1
925 AC(L3,L4) = AC(L3,L4) + AC(L1,L4)*AC(L3,L1)
930 CONTINUE
C
DN = 0.
DG = 0.
DO 1028 J1 = 1,K
AC(J1,KP2) = AC(J1,KP1)/A(J1,KP2)
J2 = KBI1 + J1
P(J2) = AMAX1(BMIN(J1),AMIN1(BMAX(J1),B(J1)+AC(J1,KP2)))
WRITE(2,4000)BMIN(J1),BMAX(J1),B(J1),AC(J1,KP2),P(J2)
4000 FORMAT(5F15.6)
DG = DG + AC(J1,KP2) * A(J1,KP1) * A(J1,KP2)
DN = DN + AC(J1,KP2) * AC(J1,KP2)
1028 AC(J1,KP2) = P(J2) - B(J1)
COSG = DG/SQRT(DN*GN)
JGAM = 0
IF ( COSG ) 1100,1110,1110
1100 JGAM = 2
COSG = - COSG
1110 CONTINUE
COSG = AMIN1(COSG,1.0)
GAMM = ARCCOS(COSG)*180./(3.14159265)
IF ( JGAM .GT. 0 ) GAMM = 180. - GAMM
1030 DO 1031 IJ=1,K
TRAN1(IJ)=P(KBI1+IJ)
1031 CONTINUE
CALL EVALU(K,TRAN1,N,TRAN2,FV)
DO 1032 IJ=1,N
P(KZI+IJ)=TRAN2(IJ)
1032 CONTINUE
1500 PHI = 0.
DO 1520 J1 = 1,N
J2 = KZI + J1
1520 PHI= PHI+(P(J2)-Y(J1))*2
IF ( PHI .LT. 1.E-10 ) GO TO 3000
IF ( I .GT. 0 ) GO TO 1540
1521 ICON = K
GO TO 2110
1540 IF ( PHI .GE. PH ) GO TO 1530
C
C EPSILON TEST
C
1200 ICON = 0
DO 1220 J1 = 1,K
J2 = KBI1 + J1
1220 IF( ABS(AC(J1,KP2))/(TAU + ABS(P(J2))) .GT. EPS ) ICON = ICON +1
IF ( ICON .EQ. 0 ) GO TO 1400
C
C GAMMA TEST
C
IF ( FL .GT. 1.0 .AND. GAMM .GT. 90.0) ICON = -1
GO TO 2105
C
C GAMMA EPSILON TEST
C
1400 IF ( FL .GT. 1.0 .AND. GAMM .LE. 45.0) ICON = -4
GO TO 2105
C
1530 IF ( I1 = 2) 1531, 1531, 2510
1531 I1 = I1 + 1
GO TO (530, 590, 800),I1

```

```
2310 IF ( FL .LT. 1.0E+8 ) GO TO 800
1320 ICON = -1
C
2105 FLA = FL
      DO 2091 J2= 1,K
      J3 = KBI1 + J2
2091 B(J2) = P(J3)
2110 DO 2050 J2 =1,N
      J3 = KZI + J2
2050 Z(J2) = P(J3)
      PH = PHI
      I = I + 1
2120 RETURN
3000 ICON = 0
      GO TO 2105
C
      END
      FUNCTION ARCOS(Z)
C
      X= Z
      KEY = 0
      IF ( X.LT. (-1.)) X = -1.
      IF ( X.GT. 1.) X= 1.
      IF ( X.GE. (-1.) .AND. X .LT. 0. ) KEY =1
      IF ( X.LT. 0.) X = ABS(X)
      IF ( X .EQ. 0. ) GO TO 10
      ARCOS = ATAN (SQRT(1. - X*X)/X)
      IF ( KEY .EQ. 1 ) ARCOS = 3.14159265 - ARCOS
      GO TO 999
10  ARCOS = 1.5707963
C
999  RETURN
      END
```



```

C
C
C
C
SUBROUTINE EVALU(NPARAM, PARAM, NPTS, XCAL2, FV)

THIS SUBROUTINE COORDINATES THE OPTIMISATION SECTION WITH THE
PROBLEM OF VAPOUR LIQUID EQUILIBRIA

0 DIMENSION TITLE(12), TCRIT(6,6), PCRIT(6,6), VCRIT(6,6),
1 OMEGA(6), IDENT(6,2), VLIQ(6), CVLIQ(6,3), PSAT(6),
2 CPSAT(6,6), CACTCO(6,6,3), GAMMA(6), X(20), Y(20), PHI(6),
3 B(6,6), F(6), FREFER(6), NREFER(6), HENRY(10,6),
4 CHENRY(10,6,2), VLIQL(10,6), CVLIQL(10,6,2), OMEGAH(6)
DIMENSION DIPOLE(6), ETA(6), X1(10)
DIMENSION PARAM(30), DATA(50,10,5), PCAL(20), XCAL2(20)
COMMON/SAI1/TITLE,NCOMP,NLIGHT,NACTCO,TCRIT,PCRIT,VCRIT,OMEGA
COMMON/SAI2/IDENT,VLIQ,CVLIQ,PSAT,CPSAT,CACTCO,GAMMA,X,SUMX,Y
COMMON/SAI3/SUMY,P,T,TOLD,PHI,B,BMIX,VMIX,ZMIX,F,FREFER,NREFER
COMMON/SAI4/HENRY,CHENRY,VLIQL,CVLIQL,OMEGAH,DIPOLE,ETA,NCRIT,X1
COMMON/SAI5/VRATIO,RT,RRT
COMMON /FLEET/ DATA, PCAL
MARK = -1
CHENRY(1,4,1) = PARAM(1)
CHENRY(1,5,1) = PARAM(2)
CACTCO(1,5,1) = PARAM(3)
CACTCO(4,5,1) = PARAM(4)
CACTCO(5,4,1) = PARAM(5)
DO 542 J = 1, NPTS
SUMX = 0.0
DO 500 K = 1, NCOMP
X(K) = DATA(J,1,K)
Y(K) = DATA(J,2,K)
SUMX = SUMX + X(K)
500 CONTINUE
P = DATA(J,3,1)
T = DATA(J,4,1)
RT = 82.057 * T
RRT = 1.9872 * T
CALL VIRIAL
CALL RSTATE
SUMY = 1.0
CALL PHIMIX(MARK)
CALL CALPLW
PCAL(J) = P
XCAL2(J) = P
DO 525 K = 1, NCOMP
DATA(J,5,K) = Y(K)
DATA(J,6,K) = F(K)
DATA(J,7,K) = GAMMA(K)
525 CONTINUE
542 CONTINUE

C
C
C
RETURN
END

```


SUBROUTINE CALPLW

C
C
C
C

SUBROUTINE TO CALCULATE TOTAL PRESSURE FROM ESTIMATED
VALUES OF THE WILSON PARAMETER AND HENRY'S CONSTANT

0 DIMENSION TITLE(12), TCRIT(6,6), PCRT(6,6), VCRIT(6,6),
1 OMEGA(6), IDENT(6,2), VLIQ(6), CVLIQ(6,3), PSAT(6),
2 CPSAT(6,6), CACTCO(6,6,3), GAMMA(6), X(20), Y(20), PHI(6),
3 B(6,6), F(6), FREFER(6), NREFER(6), HENRY(10,6),
4 CHENRY(10,6,2), VLIQL(10,6), CVLIQL(10,6,2), OMEGAH(6)
DIMENSION DIPOLE(6), ETA(6), X1(10)
COMMON/SAIL1/TITLE,NCOMP,NLIGHT,NACTCO,TCRIT,PCRT,VCRIT,OMEGA
COMMON/SAIL2/IDENT,VLIQ,CVLIQ,PSAT,CPSAT,CACTCO,GAMMA,X,SUMX,Y
COMMON/SAIL3/SUMY,P,T,TOLD,PHI,B,BMIX,VMIX,ZMIX,F,FREFER,NREFER
COMMON/SAIL4/HENRY,CHENRY,VLIQL,CVLIQL,OMEGAH,DIPOLE,ETA,NCRIT,X1
COMMON/SAIL5/VRATIO,RT,RRT
MARK = -1

C
C
C

CALCULATION OF LAMBDA'S AND ACTIVITY COEFFICIENTS

CALL ACTCO

C
C
C

CALCULATION OF PRESSURE AND VAPOUR MOLE FRACTIONS

520 DO 530 I = 1,NCOMP
F(I) = X(I)*GAMMA(I)*FREFER(I)*EXP(P*VLIQ(I)/RT)
530 CONTINUE
540 SUMY = 0.0
DO 550 I = 1,NCOMP
Y(I) = F(I) / (P*PHI(I))
SUMY = SUMY + Y(I)
550 CONTINUE

C
C
C
C

CALCULATION OF VAPOUR MOLE FRACTIONS AT CHEMICAL
EQUILIBRIUM

CALL MODCON(Y,P,T)
SUMY = 0.0
DO 552 I=1,NCOMP
SUMY = SUMY+Y(I)
552 CONTINUE
CALL PHIMIX(MARK)

C
C
C

CALCULATE SYSTEM'S TOTAL PRESSURE

POLD = P
PINT = 0.0
DO 555 I = 1,NCOMP
PINT = PINT + F(I)/PHI(I)

```

555  CONTINUE
      P = PINT
C
C    CHECK ON PRESSURE CONVERGENCE
C
      IF (ABS((POLD - P)/P) = 1.0E-4) 570,570,560
560  CALL PHIMIX(MARK)
      IF (VMIX) 590, 590, 520
570  IF (ABS(SUMY-1.0) = 1.0E-5) 590,590,580
580  CALL PHIMIX(MARK)
      IF (VMIX) 590, 590, 540
590  IF (MARK) 610, 610, 600
600  WRITE(2,923) MARK, T, P, BMIX, VMIX
      610 SUMY = 0.0
          DO 630 I = 1,NCOMP
              SUMY = SUMY + Y(I)
630  CONTINUE
      RETURN
923  FORMAT(///, 102H VOLUME SERIES VIRIAL EQUATION HAS IMAGINARY SOLUT
110NS  -- PRESSURE SERIES USED FOR FINAL CALCULATION/ 7H MARK = ,
2 14, 17H TEMPERATURE = , F7.3, 19H ' K PRESSURE = , F6.1,
315H ATM BMIX = , F10.2, 18H CC/MOL VMIX = , F9.1, 8H CC/MOL)
      END

```

MASTER COMPS

```

C
C PROGRAM FOR PARAMETER ESTIMATION OF THE ISOBARIC SYSTEM
C MAIN PROGRAM FOR NONLINEAR LEAST SQUARES FIT OF NON CONDENSABLE
C COMPONENTS LIQUID CONCENTRATION WITH HENRY'S CONSTANT AND WILSON
C PARAMETER IN THE UNSYMETRIC CONVENTION
C
C THIS PROGRAM REQUIRES THE FOLLOWING SUBROUTINES -- INPUT, VIRIAL,
C RSTATE, PHIMIX, ACTCO, CALPLW, EVALU, BMARQ, BSOLVE, MODCON
C
C ODIMENSION TITLE(12), TCRIT(6,6), PCRT(6,6), VCRIT(6,6),
C 1OMEGA(6), IDENT(6,2), VLIQ(6), CVLIQ(6,3), PSAT(6),
C 2CPSAT(6,6), CACTCO(6,6,3), GAMMA(6), X(20), Y(20), PHI(6),
C 3B(6,6), F(6), FREFER(6), NREFER(6), HENRY(10,6),
C 4CHENRY(10,6,2), VLIQL(10,6), CVLIQL(10,6,2), OMEGAH(6)
C DIMENSION DIPOLE(6), ETA(6), X1(10)
C DIMENSION PARAM(30), DATA(20,10,5), PCAL(20), DUMB(20)
C DIMENSION XLAMDA(10,10)
C COMMON/SAI1/TITLE, NCOMP, NLIGHT, NACTCO, TCRIT, PCRT, VCRIT, OMEGA
C COMMON/SAI2/IDENT, VLIQ, CVLIQ, PSAT, CPSAT, CACTCO, GAMMA, X, SUMX, Y
C COMMON/SAI3/SUMY, P, T, TOLD, PHI, B, BMIX, VMIX, ZMIX, F, FREFER, NREFER
C COMMON/SAI4/HENRY, CHENRY, VLIQL, CVLIQL, OMEGAH, DIPOLE, ETA, NCRIT, X1
C COMMON/SAI5/VRATIO, RT, RRT
C COMMON/SAI6/ XLAMDA
C COMMON /FLEET/DATA, PCAL
C CALL INPUT
C
C NPTS IS THE NUMBER OF DATA POINTS AT THE TEMPERATURE 1DEGREES
C KELVIN, NPTUNIT IS A FLAG FOR THE PRESSURE UNIT
C NPUNIT = 0, PRESSURE IN ATMOSPHERES
C NPUNIT = 1, PRESSURE IN KN/M2
C NPUNIT = 2, PRESSURE IN KG/CM2
C NPUNIT = 3 , PRESSURE IN MM HG
C
C READ(1,*) NPTS, NPARAM, NPUNIT
C
C INITIALIZATION OF PROGRAM FOR EACH DATA SET
C
C WRITE(2,901)
C NPUNIT = NPUNIT + 1
C DO 520 I=1,NPTS
C DO 511 K=1,NCOMP
C READ(1,*)(DATA(I,J,K), J=1,4)
C GO TO (511,512,515,517),NPUNIT
512 DATA(I,3,1) = DATA(I,3,1)*0.009869
C GO TO 511
515 DATA(I,3,1) = DATA(I,3,1)*0.96784
C GO TO 511
517 DATA(I,3,1) = DATA(I,3,1)*0.00131579
511 CONTINUE
520 CONTINUE
C
C INITIAL GUESS OF PARAMETERS
C
C DO 518 I =1,NPARAM
C READ(1,*) PARAM(I)
518 CONTINUE
C DO 560 I=1,NPTS

```



```

DUMP(1) = DATA(1,3,1)
560 CONTINUE
CALL BMARQ(PARAM, NPARAM, NPTS, DUMP, SQ)

C
C
C
C
FINAL PRINT OUT

DF = NPTS - NPARAM
SEE = SQRT(SQ/DF)
WRITE(2,901)
WRITE(2,912) SEE
WRITE(2,1001) IDENT(1,1), IDENT(1,2), IDENT(2,1), IDENT(2,2), T
WRITE(2,1002) TITLE
DO 548 L = 1,NCOMP
WRITE(2,902)
DO 547 M=1, NPTS
DEL = DATA(M,3,1)-PCAL(M)
WRITE(2,903)DATA(M,1,L),DATA(M,2,L),DATA(M,5,L),DATA(M,3,L),
1 PCAL(M), DEL, DATA(M,6,L), DATA(M,7,L)
547 CONTINUE
WRITE(2,1003)
548 CONTINUE
CHENRY(1,3,1) = FREFER(1)*EXP(VLIQL(1,3)*PSAT(3)/RT)
NCOM1 = NCOMP - 2
DO 801 I = 1,NCOM1
NCOM2 = I + 1
DO 802 J =NCOM2,NCOMP
WRITE(2,900)
WRITE(2,803) I,J
THETA = 0.0
DTIME = 0.0
START = 0.0
WRITE(2,904)I,J,XLAMDA(I,J),J,I,XLAMDA(J,I),CACTCO(1,J,I),
1 IDENT(J,I),IDENT(J,J),PSAT(J),CHENRY(1,J,I),PARAM(2),VLIQL(1,J),
2 IDENT(J,I),IDENT(J,J),VLIQ(J),IDENT(1,I),IDENT(1,J),R(1,I),
3 IDENT(J,I),IDENT(J,J),B(J,J)
802 CONTINUE
801 CONTINUE
WRITE(2,804) CACTCO(1,2,1), CACTCO(2,3,1), CACTCO(3,2,2)
CALL EXIT
803 FORMAT(30X, 37H INTERACTION PARAMETERS OF COMPONENT ,13,4H AND,13)
804 FORMAT(20X,50H INTERACTION PARAMETERS OF CONDENSIBLE COMPONENTS ,
1///10X,15H CACTCO(1,2,1)=, F15.6, 10X,15H CACTCO(2,3,1)=, F15.6, 1
20X,15H CACTCO(3,2,2)=, F15.6)
900 FORMAT(///)
901 FORMAT(1H1, 20X, 35HHENRY'S CONSTANT AND WILSON PARAMETER IN UNSYM
1METRIC CONVENTION FIT TO TOTAL PRESSURE )
902 FORMAT(103H X1 Y1EXP Y1CAL PEXP,ATM PCAL,ATM DELP
1 F,ATM GAMMA ///)
903 FORMAT(3F9.4, 5F9.5, F12.4, F10.4)
904 FORMAT(6HOLAMDA,2I1,2H =,F52.4/ 6H LAMDA,2I1,2H =,F52.4/,15H CACT
1CO(1,J,K)=,F48.4,4H CAL/ 23H HENRY'S CONSTANT(PSAT ,2A4, 1H=,F10.6
2, 7H ATM)=,F14.4,4H ATM / 33H HENRY'S CONSTANT(ZERO PRESSURE)=,
3F30.4, 4H ATM /, 35H MOLAR VOLUME AT INFINITE DILUTION=, F28.4, 7H
4 CC/MOL / 22H MOLAR VOLUME OF PURE , 2A4, 1H=, F2.4, 7H CC/MOL/
515H 2ND VIRIAL OF , 2A4, 1H=, F39.4, 7H CC/MOL / 15H 2ND VIRIAL OF
6 , 2A4, 1H=, F39.4, 7H CC/MOL ///////////////)
912 FORMAT(48H COMPARISON OF INPUT DATA AND CALCULATED RESULTS/
130H STANDARD ERROR OF ESTIMATE = , E20.8, 5X, 38H ABSOLUTE PER CEN
2T ERROR IN PRESSURE ///)
1001 FORMAT(///25X, 7HSYSTEM , 2A4, 1H=, 2A4, 4H AT , F8.2, 7H DEG K//
1/)
1002 FORMAT(20X, 12A6, ///)
1003 FORMAT(1H1)
END

```

APPENDIX VIII

COMPUTER PROGRAMS FOR DISTILLATION

CALCULATION

Listing of programs for the calculation of distillation with chemical reaction are given in this appendix. The listing includes the following segments;

1. Subroutine NEWTON
2. Subroutine GAUSS
3. Subroutine HTCNT
4. Subroutine EFFICIENCY
5. Subroutine PRINT
6. Subroutine WPRINT
7. Subroutine BUBLDILF (Version B)
8. Subroutine INPUT (Version B)
9. Program CHEMICOL.


```

SUBROUTINE NEWTON(M,N,XA,XB,XC,XD,XE,XF,XG,XH,XI,ITER)
C
C  NEWTON RAPHSON METHOD FOR SOLUTION OF NON LINEAR
C  SIMULTANEOUS EQUATIONS
C
  DIMENSION A(10,10), B(10), Y(10), X(10)
  DIMENSION C(15), Z(4), ZF(6), ZX(6), Z1(6), AC(5)
  COMMON/TRAY14/C,Z,ZF,ZX,Z1,AC,DRL1,DRL2
C
C  SETTING THE COEFFICIENTS OF LINEARIZED EQUATIONS
C  IN MATRIX FORM
C
  X(1) = XA
  X(2) = XB
  X(3) = XC
  X(4) = XD
  X(5) = XE
  X(6) = XF
  X(7) = XG
  X(8) = XH
  X(9) = XI
  DO 5 I=1,5
    IF(X(I) .LT. 0.0) X(I) = 0.01
  5  CONTINUE
  DO 40 I=1,N
    DO 20 J=1,N
      DO 10 J1=1,N
        A(J,J1) = 0.0
      10  CONTINUE
    20  CONTINUE
    A(1,1) = AC(1)*X(3)
    A(1,2) = AC(2)*X(3)
    A(1,3) = AC(3)*X(3)
    A(1,4) = AC(4)*X(3)
    A(1,5) = AC(5)*X(3)
    A(1,6) = -DRL1
    A(1,7) = -DRL2
    A(1,8) = AC(1)*X(1)+AC(2)*X(2)+AC(3)*X(3)+AC(4)*X(4)+AC(5)*X(5)
    A(1,9) = -C(1)
    A(2,1) = 1.0
    A(2,4) = -C(2)
    A(3,1) = -C(3)*X(3)
    A(3,2) = 1.0
    A(3,3) = -C(3)*X(1)
    A(4,1) = 1.0
    A(4,2) = 1.0
    A(4,3) = 1.0
    A(4,4) = 1.0
    A(4,5) = 1.0
    A(5,1) = X(8)

```

```

A(5,6) = -1.0
A(5,7) = -1.0
A(5,8) = X(1)
A(5,9) = -Z(1)
A(6,2) = X(3)
A(6,7) = 1.0
A(6,8) = X(2)
A(6,9) = -Z(2)
A(7,3) = X(3)
A(7,7) = -1.0
A(7,8) = X(3)
A(7,9) = -Z(3)
A(8,4) = X(8)
A(8,6) = 1.0
A(8,8) = X(4)
A(8,9) = -Z(4)
A(9,5) = X(3)
A(9,6) = -1.0
A(9,8) = X(5)
A(9,9) = -Z(5)
B(1) = -AC(1)*X(3)*Y(1)-AC(2)*X(8)*X(2)-AC(3)*X(8)*X(3)
1-AC(4)*Y(3)+X(4)-AC(5)*X(8)*X(5)+C(1)*X(9)+DRL1*X(6)+DRL2*X(7)
2-C(4)*C(5)-C(6)*C(7)+C(8)*C(9)-C(10)
B(2) = -X(1)+C(2)*X(4)
B(3) = -X(2)+C(3)*X(1)*Y(3)
B(4) = -X(1)-X(2)-X(3)-X(4)-X(5)+1
B(5) = -X(3)*X(1)+Z(1)*X(9)+X(6)+X(7)-C(4)*Z1(1)-C(6)*ZF(1)
1+C(8)*ZX(1)
B(6) = -X(8)*X(2)+Z(2)*Y(9)-X(7)-C(4)*Z1(2)-C(6)*ZF(2)
1+C(8)*ZX(2)
B(7) = -X(8)*X(3)+Z(3)*X(9)+X(7)-C(4)*Z1(3)-C(6)*ZF(3)
1+C(8)*ZX(3)
B(8) = -X(8)*X(4)+Z(4)*X(9)-X(6)-C(4)*Z1(4)-C(6)*ZF(4)
1+C(8)*ZX(4)
B(9) = -X(8)*X(5)+Z(5)*X(9)+X(6)-C(4)*Z1(5)-C(6)*ZF(5)
1+C(8)*ZX(5)

C
C      SOLUTION OF LINEARIZED EQUATIONS
C
      CALL GAUSS(N,A,B,Y)
      I9 = 1
      DO 30 I1=1,N

C
C      CHECK ON CONVERGENCE
C
      IF(ABS(Y(I1)) .GT. C(11)) I9 = 0
      X(I1) = X(I1)+Y(I1)
30  CONTINUE
      IF(I9.EQ. 0) GO TO 40
      GO TO 60
40  CONTINUE
      WRITE(2,50) M
50  FORMAT(10X,32H CONVERGENCE WAS NOT ACHIEVED IN ,I5,
111H ITERATIONS )
      STOP
60  ITER=I
      XA = X(1)
      XB = X(2)
      XC = X(3)
      XD = X(4)
      XE = X(5)
      XF = X(6)
      XG = X(7)
      XH = X(8)
      XI = X(9)
      RETURN
      END

```

```

SUBROUTINE GAUSS(N,A,B,Y)
C
C  GAUSS ELIMINATION TECHNIQUE FOR SOLUTION OF
C  SIMULTANEOUS LINEAR EQUATIONS
C
  DIMENSION A(10,10), B(10), Y(10)
  N1 = N-1
  DO 50 K=1,N1
    K1 = K+1
    L = K
    DO 10 I1=K1,N
      IF(ABS(A(I1,K))-ABS(A(L,K))) 10,10,5
5    L = I1
10  CONTINUE
    IF(L=K) 25, 25, 15
15  DO 20 J=1,N
    T = A(K,J)
    A(K,J) = A(L,J)
    A(L,J) = T
20  CONTINUE
    T = B(K)
    B(K) = B(L)
    B(L) = T
25  DO 40 I1 =K1,N
    F = A(I1,K)/A(K,K)
    A(I1,K) = 0.0
    DO 30 J=K1,N
      A(I1,J) = A(I1,J)-F*A(K,J)
30  CONTINUE
    B(I1) = B(I1)-F*B(K)
40  CONTINUE
50  CONTINUE
    DO 60 K=1,N
      IF(A(K,K).EQ. 0.0) GO TO 100
60  CONTINUE
      Y(N) = B(N)/A(N,N)
      I1 = N1
65  I2 = I1+1
      S = 0.0
      DO 70 J=I2,N
        S = S+A(I1,J)*Y(J)
70  CONTINUE
      Y(I1) = (B(I1)-S)/A(I1,I1)
      I1 = I1-1
      IF(I1) 80, 80, 65
80  CONTINUE
      RETURN
100 WRITE(2,200)
200 FORMAT(10X,30H EQUATIONS ARE ILL CONDITIONED )
      STOP
      END

```

```
      SUBROUTINE HTCNT(X, NCOMP, HT, T, FL, HTP)
C
C      SUBROUTINE FOR CALCULATION OF VAPOUR AND LIQUID
C      PHASE ENTHALPIES
C
      DIMENSION X(5), DHV(6), HTP(5)
      COMMON /TRAY1/A(10),B(10),C(10),D(10)
      COMMON/TRAY11/TREF
      COMMON/TRAY13/DHV
      LOGICAL FL
      HT=0.0
C
C      VAPOUR PHASE ENTHALPIES
C
      DO 100 I=1,NCOMP
      HTP(I) = D(I)*A(I)*(T-TREF)+B(I)*(T**2-TREF**2)/2.0
1+C(I)*(T**3-TREF**3)/3.0
      IF(FL) GO TO 90
C
C      LIQUID PHASE ENTHALPIES
C
      HTP(I) = HTP(I)-DHV(I)
90    CONTINUE
C
C      ENTHALPY OF THE MIXTURE
C
      HT = HT+X(I)*HTP(I)
100  CONTINUE
      RETURN
      END
```


SUBROUTINE EFFICIENCY(I, VMIX)

SUBROUTINE FOR CALCULATION OF EFFICIENCY
USING A.I.C.H.E. MANUAL'S METHOD

DIMENSION XR(6,15), YR(6,15), XRF(6,15), FFD(15), FVAPR(15)
DIMENSION FLIQR(15), ALFA(15), BETA(15), ITER(15), V(15)
DIMENSION UM(6), TUNL(6), TUNV(6), VQ(6), TB(6), VCRT(6)
DIMENSION GRAD(6), VISV(6), TU(6), PEFF(6), EFF(6,15)
DIMENSION TETA(6,1), ALAM(6), X2(10), Y3(20), VLIQ1(6)
DIMENSION VIS(6), SHW(6), DIFL(6), DIFV(6), DIV(6,6), YR2(6,15)
DIMENSION DIEF(6,6)
DIMENSION T(15), TF(15)
COMMON/TPAY3/IFID, XTRAY, ITRAY, NCOMP, TF, T, XR, YR, XRF
COMMON/TPAY9/FFD, FVAPR, FLIQR, ALFA, BETA, ITER, IS
COMMON/TPAY10/FLPRD, REFLXR, V, DN
COMMON/TPAY15/UM, VQ, TB, VCRT, NEF, DIEF, RFT
COMMON/TPAY16/VLIQ1, X2, YR2
COMMON/TPAY17/EFF
IF(I.NE.1) GO TO 4
DO 4 IM=1,NCOMP

CALCULATION OF ACTUAL VAPOUR PHASE MOLE FRACTIONS
FOR BOILER STAGE USING VAPORIZATION EFFICIENCY

YR(IM,I) = RFT*(YR2(IM,I)-XR(IM,I))+XR(IM,I)
EFF(IM,I) = RFT
4 CONTINUE
GO TO 135
5 CONTINUE
SUM = 0.0

EVALUATION OF PARAMETERS FOR EFFICIENCY CALCULATIONS

UG = VMIX*FVAPR(1)/(100.0*45.603)
DO 10 IJ=1,NCOMP
IF(IS.EQ.1) YR(IJ,I) = YR2(IJ,I)
SUM = SUM+YR(IJ,I)*UM(IJ)
10 CONTINUE
RG = SUM*1000.0/VMIX
EFFCT = UG*RG**0.5
WMIX = 0.0
DO 20 IJ=1,NCOMP
WMIX = WMIX+VLIQ1(IJ)*X2(IJ)
20 CONTINUE
ELL = WMIX*FLIQR(1)/44400.0
DO 30 IJ=1,NCOMP
GRAD(IJ) = (YR2(IJ,I-1)-YR2(IJ,I))/(XR(IJ,I-1)-X2(IJ))
ALAM(IJ) = ABS(GRAD(IJ))*FVAPR(1)/FLIQR(1)


```

30  CONTINUE
    HF = 0.0354+4.81*ELL/60.0+1.05*V(I)/100.0+0.0384*UG/60.0
    HL = 0.024+1.74*ELL/60.0+0.372*V(I)/100.0+0.012*UG/60.0
    TL = 4560.36*HL*60.0/(FLIQR(I)*WMIX)

C
C    LIQUID PHASE VISCOSITY
C
    VIS(1) = 17.2498E-3*EXP(674.4039/T(I))
    VIS(2) = 106.5788E-3*EXP(292.0666/T(I))
    VIS(3) = 9.1946E-3*EXP(1219.2063/T(I))
    VIS(4) = 65.4943E-3*EXP(677.8923/T(I))
    VIS(5) = 1.791E-3*EXP(1851.68/T(I))
    B = 0.166104
    B1 = 1.0/B
    VISCL = (0.161788*69.9404*X2(1)*VIS(1)**B-13.6794*X2(2)
1*VIS(2)**B+3.13164*X2(3)*VIS(3)**B+1.31778*X2(4)*VIS(4)
2**B+0.873686*X2(5)*VIS(5)**B)**B1
    DO 50 IJ=1,NCOMP

C
C    LIQUID PHASE DIFFUSIVITY
C
    SUM = 0.0
    SUM1 = 0.0
    DO 40 JJ=1,NCOMP
    IF(IJ.EQ.JJ) GO TO 40
    SUM = SUM+X2(JJ)
    SUM1 = SUM1+X2(JJ)*WM(JJ)
40  CONTINUE
    SMW(IJ) = SUM1/SUM
    DIFL(IJ) = 7.4E-8*T(I)*SMW(IJ)**0.5/(VISCL*V0(IJ)**0.6)

C
C    LIQUID PHASE TRANSFER UNIT
C
    TUNL(IJ) = 100.0*(3.875*DIFL(IJ))**0.5*(0.0066945*FFCT
1+0.17)*TL
50  CONTINUE

C
C    VAPOUR PHASE VISCOSITY
C
    DO 60 IJ=1,NCOMP
    SIG = 0.833*VCRT(IJ)**0.3333
    TKE = T(I)/(1.39*TB(IJ))
    ROMG = 1.17183+2.86572*EXP(-1.93766*TKE)
    VISV(IJ) = 0.0026693*(WM(IJ)*T(I))**0.5/(SIG**2*ROMG)
60  CONTINUE
    VISCV = 0.0
    DO 80 II=1,NCOMP
    SUM = 1.0
    DO 70 JJ=1,NCOMP
    IF(II.EQ.JJ) GO TO 70
    TETA(II,JJ) = (1.0+(VISV(II)/VISV(JJ))**0.5*(WM(JJ)/WM
1(II))**0.25)**2/(2.0*2.0**0.5*(1.0*WM(II)/WM(JJ))**0.5)
    SUM = SUM+TETA(II,JJ)*YR(JJ,I)/YR(II,I)
70  CONTINUE
    VISCV = VISCV+VISV(II)/SUM
80  CONTINUE

C
C    VAPOUR PHASE DIFFUSIVITY
C
    DO 120 II=1,NCOMP
    IF(II.EQ.NEF) GO TO 120
    SUM = 0.0
    DO 90 JJ=1,NCOMP
    IF (II.EQ.JJ) GO TO 90
    B = 0.00107-0.000246*(1.0/WM(II)+1.0/WM(JJ))**0.5
    DIA = 1.18*(V0(II)**0.3333+V0(JJ)**0.3333)/2.0

```

```

TKE = (T(I)/(1.15*TB(II))*T(I)/(1.15*TB(JJ)))*0.5
BOMG = 0.55779+1.45741*EXP(-2.21371*TKE)
DIV(II,JJ) = B*T(I)**1.5*(1.0/WM(II)+1.0/WM(JJ))*0.5
1/(PN*DIA**2*BOMG)
SUM = SUM+YR(JJ,I)/DIV(II,JJ)
90 CONTINUE
DIFV(II) = (1.0-YR(II,I))/SUM

C
C VAPOUR PHASE TRANSFER UNIT
C
TUNV(II) = (RG*DIFV(II)/(10.0*VISCV))*0.5*(0.776+0.0457
1*V(I)-0.238*FFCT/60.0+1.75*ELL)
TU(II) = 1.0/(1.0/TUNV(II)+ALAM(II)/TUNL(II))

C
C POINT EFFICIENCY
C
PEFF(II) = 1.0-EXP(-TU(II))
DE = 0.0929*(0.0124+0.0561*UG/60.0+0.202*ELL+0.00591*V(I))*2
PE = (3.0*2.54)**2/(10000.0*DE*TL)
ETA = PE*((1.0+4.0*ALAM(II)*PEFF(II)/PE)**0.5-1.0)/2.0
IF (ABS(ETA+PE).GT. 30.0) GO TO 100
A = EXP(-ETA-PE)
GO TO 110
100 A = 0.0
110 RTO = (1.0-A)/((ETA+PE)*(1.0+(ETA+PE)/ETA))+(EXP(ETA)
1-1.0)/(ETA*(1.0+ETA/(ETA+PE)))

C
C EFFICIENCY CALCULATIONS AND MODIFICATION
C TO CALCULATED EFFICIENCIES
C
IF(I.LT.ITRAY) MN = 1
IF(I.GE.ITRAY) MN = 2
EFF(II,I) = RTO*PEFF(II)+DIEF(MN,II)
120 CONTINUE
SUM = 0.0
DO 130 II=1,NCOMP
IF(II,EQ,NEF) GO TO 130

C
C CALCULATION OF ACTUAL VAPOUR PHASE MOLE FRACTIONS
C
YR(II,I) = EFF(II,I)*(YR2(II,I)-YR(II,I-1))+YR(II,I-1)
SUM = SUM+YR(II,I)
130 CONTINUE
YR(NEF,I) = 1.0-SUM
EFF(NEF,I) = (YR(NEF,I)-YR(NEF,I-1))/(YR2(NEF,I)-YR(NEF,I-1))
135 CONTINUE
DO 140 II=1,NCOMP
Y3(II) = YR(II,I)
140 CONTINUE
CALL MODCON(Y3, PN, T(I))
DO 150 II=1,NCOMP
YR(II,I) = Y3(II)
150 CONTINUE
RETURN
END

```

```

SUBROUTINE PRINT
C
C SUBROUTINE TO PRINT INTERMEDIATE AND FINAL RESULTS
C
  DIMENSION CODE(12),TITLE(12),FFD(15),TF(15),XRF(6,15),YR(6,15)
  DIMENSION XR(6,15),FVAPR(15),FLIQR(15),T(15),ALFA(15),BETA(15)
  DIMENSION V(15),ITER(15)
  DIMENSION EFF(6,15)
  COMMON/TRAY7/CODE,TITLE
  COMMON/TRAY8/IFIN,NTRAY,ITRAY,NCOMP,TF,T,XR,YR,XRF
  COMMON/TRAY9/FFD,FVAPR,FLIQR,ALFA,BETA,ITER,IS
  COMMON/TRAY10/FLPRO,REFLXR,V,PN
  COMMON/TRAY17/EFF
  WRITE(2,1)
  1  FORMAT(1H1)
C
C PRINT HEADINGS
C
  WRITE(2,203)CODE
  203  FORMAT(20X,12A6,10X, 8H CHEMCOL )
  WRITE(2,2) TITLE
  2  FORMAT(20X,31H COMPONENTS UNDER DISTILLATION //,20X,12A6)
  WRITE(2,300) IS
  300  FORMAT(20X,24H TOTAL NO OF ITERATIONS= ,15)
  IF(IFIN.EQ.0) GO TO 5
  WRITE(2,3)
  3  FORMAT(50X,13H FINAL RESULT )
  5  DO 140 I=1,NTRAY
  WRITE(2,10)I
  10  FORMAT(20X,11H STAGE NO. ,13)
  WRITE(2,301) ITER(I)
  301  FORMAT(20X,27H NO OF INTERNAL ITERATIONS= ,15 )
  DO 12 IP=1,NCOMP
  WRITE(2,13)IP, EFF(IP,I)
  12  CONTINUE
  13  FORMAT(10X,11H EFFICIENCY ,13,2X,F12.8)
  II=I+1
  II=I-1
  IF(I.EQ.NTRAY) GO TO 100
  IF(I.EQ.1) GO TO 80
  IF(I.EQ.ITRAY) GO TO 20
  GO TO 40
C
C FEED STAGE PRINT OUT
C
  20  WRITE(2,30) FFD(I), TF(I)
  30  FORMAT(20X,11H FEED PLATE / 15X,15H FEED FLOW RATE,F10.6,11H GRAMM
  1S/MIN,5X,10H FEED TEMP ,F10.4,6H DEG.K /30X,24H FEED COMPOSITIONS
  2MOLEX )
  DO 35 J=1,NCOMP
  WRITE(2,32) J, XRF(J,ITRAY)
  32  FORMAT(35X,4H XF(,12,3H )=,F6.4)
  35  CONTINUE
C
C STAGE PRINT OUT
C
  40  WRITE(2,50) II,FVAPR(II),II1,FLIQR(II1)
  50  FORMAT(10X,52H FLOW RATES OF CURRENTS ENTERING THE STAGE MOLES/MIN
  1 /10X,3H V(,12,3H )=,F10.6,10X,3H L(,12,3H )=,F10.6/20X,32H CONCE
  2NTRATION OF CURRENTS MOLEX )
  DO 55 J=1,NCOMP
  WRITE(2,52)J,II,YR(J,II),J,II1,XR(J,II1)
  52  FORMAT(25X,3H Y(,12,2H ,,12,3H )=,F6.4,20X,3H X(,12,2H ,,12,3H )=,
  1F6.4/ )
  55  CONTINUE

```



```

56  CONTINUE
    WRITE(2,60) I, FVAPR(I), I, FLIQR(I)
60  FORMAT(10X, 51H FLOW RATES OF CURRENTS LEAVING THE STAGE MOLES/MIN/
110X, 3H V(, 12, 3H )=, F10.6, 10X, 3H L(, 12, 3H )=, F10.6/20X, 32H CONCENTR
2ATION OF CURRENTS MOLE% )
    DO 65 J=1, NCOMP
    WRITE(2,62) J, I, YR(J, I), J, I, XR(J, I)
62  FORMAT(25X, 3H Y(, 12, 2H , , 12, 3H )=, F6.4, 20X, 3H X(, 12, 2H , , 12, 3H )=,
1F6.4/ )
65  CONTINUE
    GO TO 130

C
C   BOILER STAGE PRINT OUT
C
80  WRITE(2,85)
85  FORMAT(20X, 14H BOILER STAGE )
    WRITE(2,90) II, FLIQR(II)
90  FORMAT(10X, 52H FLOW RATES OF CURRENTS ENTERING THE STAGE MOLES/MIN
1/30X, 3H L(, 12, 3H )=, F10.6/20X, 32H CONCENTRATION OF CURRENTS MOLE% )
    DO 95 J=1, NCOMP
    WRITE(2,92) J, II, XR(J, II)
92  FORMAT(30X, 3H X(, 12, 2H , , 12, 3H )=, F6.4/ )
95  CONTINUE
    GO TO 56

C
C   CONDENSER STAGE PRINT OUT
C
100 WRITE(2,105)
105 FORMAT(20X, 16H CONDENSER STAGE )
    WRITE(2,110) II, FVAPR(II)
110 FORMAT(10X, 52H FLOW RATES OF CURRENTS ENTERING THE STAGE MOLES/MIN
1/10X, 3H V(, 12, 3H )=, F10.6/20X, 32H CONCENTRATION OF CURRENTS MOLE% )
    DO 115 J=1, NCOMP
    WRITE(2,112) J, II, YR(J, II)
112 FORMAT(25X, 3H Y(, 12, 2H , , 12, 3H )=, F6.4/ )
115 CONTINUE
    WRITE(2,120) I, FLIQR(I)
120 FORMAT(10X, 51H FLOW RATES OF CURRENTS LEAVING THE STAGE MOLES/MIN/
126X, 3H L(, 12, 3H )=, F10.6/20X, 32H CONCENTRATION OF CURRENTS MOLE% )
    DO 125 J=1, NCOMP
    WRITE(2,122) J, I, XR(J, I)
122 FORMAT(50X, 3H X(, 12, 2H , , 12, 3H )=, F6.4/ )
125 CONTINUE
130 WRITE(2,132) ALFA(I), BETA(I)
132 FORMAT(40X, 37H NO. OF MOLES REACTED IN LIQUID PHASE /20X, 11H REACT
1ION 1, F6.4, 10X, 11H REACTION 2, F6.4)
    IF(I.NE.NTRAY) GO TO 136
    WRITE(2,200) FLPRO, T(NTRAY)
200 FORMAT(10X, 33H CALCULATED TOP PRODUCT MOLES/MIN, F10.6, 10X, 14H PRO
1DUCT TEMP., F10.6, /10X, 29H PRODUCT CONCENTRATIONS MOLE% )
    WRITE(2,201) (II, XR(II, NTRAY), II=1, NCOMP)
201 FORMAT(5X, 6(3H X(, 12, 3H )=, F6.4, 5X))
    WRITE(2,202) REFLXR
202 FORMAT(20X, 25H CALCULATED REFLUX RATIO, F10.4)
133 WRITE(2,135) V(I)
135 FORMAT(20X, 25H STAGE VOLUME HOLD UP CC, F10.6, /11H)
    GO TO 140
136 WRITE(2,250) T(I)
250 FORMAT(10X, 25H TEMPERATURE OF THE STAGE, F10.4)
    GO TO 133
140 CONTINUE
    IF(IFIN.NE.0) CALL WPRINT
    RETURN
    END

```

```

SUBROUTINE WPRINT
C
C SUBROUTINE TO PRINT RESULTS IN WEIGHT PERCENTS
C FOR THE ORIGINAL COMPONENTS;
C FORMALDEHYDE, METHANOL AND WATER
C
  DIMENSION TF(15), T(15), XR(6,15), YR(6,15), XRF(6,15)
  DIMENSION WM(6), VO(6), TB(6), VCRT(6)
  DIMENSION DIEF(6,6)
  COMMON/TRAY8/IFIN,NTRAY,I,TRAY,NCOMP,TF,T,XR,YR,XRF
  COMMON/TRAY15/WM, VO, TB, VCRT, NEF, DIEF, BFT
  WRITE(2,100)
  DO 50 I=1,NTRAY
C
C CONVERSION OF MOLE FRACTIONS TO WEIGHT FRACTIONS
C
    A = (XR(1,I)+XR(2,I)+XR(4,I))*WM(1)
    B = (XR(2,I)+XR(3,I))*WM(3)
    C = (XR(4,I)+XR(5,I))*WM(5)
    E = (YR(1,I)+YR(2,I)+YR(4,I))*WM(1)
    F = (YR(2,I)+YR(3,I))*WM(3)
    G = (YR(4,I)+YR(5,I))*WM(5)
    D = A+B+C
    H = E+F+G
    A = A/D
    B = B/D
    C = C/D
    IF(I.EQ,NTRAY) GO TO 40
    E = E/H
    F = F/H
    G = G/H
  40  CONTINUE
    WRITE(2,200)I, T(I), A, B, C, E, F, G
  50  CONTINUE
  100  FORMAT(1H1,5X,10H STAGE NO. ,1X,5H TEMP ,3X,5H X(1), 3X,5H X(2),
1 3X,5H X(3),3X,5H Y(1),3X,5H Y(2),3X,5H Y(3))
  200  FORMAT(9X,I2,5X,F6.2,6(2X,F6.4))
    RETURN
    END

```


CCCCCCCC

```

CALL ACTCO
TOLD = T
SUMY = 0.0
DO 550 I=1,NCOMP
F(I) = X1(I) * GAMMA(I) * PREFER(I) * EXP(VLIQ(I) * P / RT)
Y(I) = F(I) / (P*PHI(I))
SUMY = SUMY + Y(I)
YM(I) = Y(I)
550 CONTINUE
CALL MODCON(YM,P,T)
SUMY = 0.0
DO 551 I=1,NCOMP
Y(I) = YM(I)
SUMY = SUMY+Y(I)
551 CONTINUE
PINT = 0.0
DO 555 I=1,NCOMP
PINT = PINT+F(I)/PHI(I)
555 CONTINUE
PINTO = PINT
MARK = -1

C
C BEGIN AN ITERATION TO FIND VAPOUR PHASE FUGACITY COEFFICIENTS
C
560 CALL PHIMIX(MARK)
IF(VMIX) 650, 650, 565
565 KOUNT = KOUNT +1
SUMY = 0.0
DO 570 I=1,NCOMP
Y(I) = F(I) / (P*PHI(I))
SUMY = SUMY + Y(I)
YM(I) = Y(I)
570 CONTINUE
CALL MODCON(YM,P,T)
SUMY = 0.0
DO 571 I=1,NCOMP
Y(I) = YM(I)
SUMY = SUMY+Y(I)
571 CONTINUE
PINT = 0.0
DO 575 I=1,NCOMP
PINT = PINT + F(I)/PHI(I)
575 CONTINUE

C
C CHECK TO SEE WHETHER PRESSURE IS CONSTANT
C
IF(ABS(PINT-PINTO)/PINT-1,0E-4) 590, 590, 580
580 PINTO = PINT
GO TO 560

C
C CHECK FOR THE CONVERGENCE OF CALCULATED PRESSURE
C TO ACTUAL PRESSURE
C
590 SUMY1 = PINT - P
THETA = 0.0
IF (ABS(SUMY1)-1,0E-4) 650, 650, 595
595 IF (TPREV) 600, 600, 615
600 PINTP = PINT
TPREV = T
IF (SUMY1) 605, 650, 610
605 T = T * 1.020
GO TO 540
610 T = T * 0.980
GO TO 540

C
C ADJUST THE TEMPERATURE AND START ANOTHER ITERATION

```

```

C
615 SLOPE = (T-TPREV)/(PINT-PINTP)
    PINTP = PINT
    TPREV = T
    DELT = SLOPE*SUHYY1
    IF (ABS (DELT) - .1 * T) 625, 625, 620
620 DELT = SIGN(.1 * T, DELT)
625 T = T - DELT
    GO TO 540
650 CONTINUE
    IF (MARK) 660, 655, 655
655 WRITE(2,923)

C
C      ADJUSTMENT OF VAPOR COMPOSITION AND TEMPERATURE
C      FOR SOLUTIONS WITH METHANOL CONTENT OF 0.01 TO 0.12
C
660 IF(X1(3) .GE. 0.12 .OR. X1(3) .LT. 0.01) GO TO 700
    XDM1 = (X1(1)+X1(2)+X1(4))/(1.0+X1(2)+X1(4))
    XDM3 = (X1(2)+X1(3))/(1.0+X1(2)+X1(4))
    XDM5 = (X1(4)+X1(5))/(1.0+X1(2)+X1(4))
    YDM1 = (Y(1)+Y(2)+Y(4))/(1.0+Y(2)+Y(4))
    YDM3 = (Y(2)+Y(3))/(1.0+Y(2)+Y(4))
    YDM5 = (Y(4)+Y(5))/(1.0+Y(2)+Y(4))
    T = T+3.0
    YM(1) = YDM1-0.144931*XDM1**0.341386+0.943512*XDM2**
11.50803+0.016604
    YM(2) = 0.0
    YM(3) = YDM3+0.514268*XDM1**0.797498+0.905221*XDM3**
10.034031+0.18591*XDM5**5-0.955265
    YM(4) = 0.0
    YM(5) = YDM5+0.222355*XDM1**0.176251+0.839034*XDM3**
1(-0.0211675)+0.0931838*XDM5**2.28577-1.10191
    CALL MODCON(YM, P, T)
    DO 670 I=1,NCOMP
    Y(I) = YM(I)
670 CONTINUE
700 DO 710 I=1,NCOMP
    YK(I) = Y(I)
    XK(I) = X1(I)
710 CONTINUE
    TK = T

C
C      COORDINATION OF EFFICIENCY CALCULATION
C
    DO 711 I=1,NCOMP
    VLIQ1(I1) = VLIQ(I1)
    X2(I1) = X1(I1)
711 CONTINUE
    IF(EFFG) GO TO 730
    DO 720 I=1,NCOMP
    EFF(I,IT) = 1.0
    IF(IT.EQ.NTRAY) GO TO 720
    YR2(I,IT) = Y(I)
720 CONTINUE
    GO TO 750
730 DO 740 I=1,NCOMP
    YR2(I,IT) = Y(I)
740 CONTINUE

C
C      EFFICIENCY CALCULATION
C
    CALL EFFICIENCY(IT, VMIX)
750 CONTINUE

C
C      CALCULATION OF HEAT OF VAPOURIZATION AS A
C      FUNCTION OF TEMPERATURE

```


C

```

DHV(1) = 7950.62*(1.0-T/TCRIT(1,1))*0.38
DHV(2) = 7576.247*(1.0-T/TCRIT(2,2))*0.38
DHV(3) = 12318.642*(1.0-T/TCRIT(3,3))*0.38
DHV(4) = 6292.812*(1.0-T/TCRIT(4,4))*0.38
DHV(5) = 13206.043*(1.0-T/TCRIT(5,5))*0.38
RETURN
923 FORMAT(///,102H VOLUME SERIES VIRIAL EQUATION HAS IMAGINARY SOLUTI
10NS -- PRESSURE SERIES USED FOR FINAL CALCULATIONS )
END
```

SUBROUTINE INPUT

```

C
C SUBROUTINE TO READ IN ALL PURE COMPONENT DATA AND BINARY
C INTER ACTION PARAMETERS
C
DDIMENSION TITLE(12), TCRIT(6,6), PCRT(6,6), VCRIT(6),
1OMEGA(6), IDENT(6,2), VLIQ(6), CVLIQ(6,3), PSAT(6),
2CPSAT(6,6), CACTCO(6,6,3), GAMMA(6), X(10,10), Y(10), PHI(6),
4CHENRY(10,6,2), VLIQL(10,6), CVLIQL(10,6,2), OMEGAH(6),
3B(6,6), F(6), FREFER(6), NREFER(6), HENRY(10,6)
DIMENSION DIPOLE(6), ETA(6), X1(10)
DIMENSION WM(6), VO(6), TB(6), VCRT(6)
DIMENSION COMPI(6,6), CORF(6,6), FACT(6), DIEF(6,6)
COMMON/TRAY2/TITLE, NCOMP, NLIGHT, NACTCO, TCRIT, PCRT, VCRIT, OMEGA
COMMON/TRAY3/IDENT, VLIQ, CVLIQ, PSAT, CPSAT, CACTCO, GAMMA, X, SUMX, Y
COMMON/TRAY4/SUMY, P, T, TOLD, PHI, B, BHIX, VMIX, ZMIX, F, FREFER, NREFER
COMMON/TRAY5/HENRY, CHENRY, VLIQL, CVLIQL, OMEGAH, DIPOLE, ETA, NCRIT, X1
COMMON/TRAY15/WM, VO, TB, VCRT, NEF, DIEF, BFT
COMMON/FLEET/IFLG
IFLG=IFLG+1
READ(1,901)TITLE
READ(1,902)NCOMP, NLIGHT, NACTCO

C
C NCOMP = TOTAL NO. OF COMPONENTS, NLIGHT = NO OF COMPONENTS TREATED
C IN THE UNSYMMETRIC CONVENTION.
C NACTCO = NO. OF BINARY INTERACTION PARAMETERS PER PAIR
C
C NOTE - ARRANGE PURE COMPONENTS DATA IN ORDER OF INCREASING
C CRITICAL TEMPERATURE
C
NACTCO = (NACTCO + 1) / 2
N1 = NLIGHT + 1
NCOMP1 = NCOMP - 1

C
C READ IN PURE COMPONENT PROPERTIES - THREE CARDS FOR EACH SPECIES
C 1 - CRITICAL PROPERTIES / 2 - LIQUID VOLUMES / 3 - VAPOR PRESSURES
C FOR SUPERCRITICAL COMPONENTS ONLY THE INFORMATION ON THE FIRST
C CARD IS USED.
C
DO 90 I=1, NCOMP
C READ (1,903) TCRIT(I,1), PCRT(I,1), VCRIT(I), OMEGA(I), OMEGAH(I),
1DIPOLE(I), ETA(I), IDENT(I,1), IDENT(I,2)
IF(DIPOLE(I)) 33, 33, 36
33 OMEGAH(I) = OMEGA(I)
36 READ(1,904) T1, V1, T2, V2, T3, V3
READ(1,904) (CPSAT(I,J), J=1,6)
39 IF(T3) 40,40,77
40 CVLIQ(I,3) = 0.0
IF(T2) 50,50,60
50 CVLIQ(I,2) = 0.0

```



```

      CVLIQ(I,1) = V1
      GO TO 90
60  CVLIQ(I,2) = (V2-V1)/(T2-T1)
      CVLIQ(I,1) = V1-CVLIQ(I,2)*T1
      GO TO 90
700 CVLIQ(I,3) = ((T3-T1) * (V2-V1) - (V3-V1) * (T2-T1)) / ((T
      12**2 - T1**2) * (T3-T1) - (T3**2 - T1**2) * (T2-T1))
      CVLIQ(I,2) = ((V2-V1)-CVLIQ(I,3)*(T2**2-T1**2))/(T2-T1)
      CVLIQ(I,1) = V1-CVLIQ(I,2)*T1-CVLIQ(I,3)*T1**2
90  CONTINUE

C
C      CALCULATE CRITICAL PROPERTIES FOR BINARY INTERACTIONS
C
      DO 110 I=1,NCOMP1
      DO 100 J=1,NCOMP1
      TCRIT(I,J)=SQRT(TCRIT(I,I)*TCRIT(J,J))
      PCRIT(I,J) = 4.0 * TCRIT(I,J) * (PCRIT(I,I) * VCRIT(I) / TCRIT(I,I)
      1) + PCRIT(J,J) * VCRIT(J) / TCRIT(J,J)) / (VCRIT(I)**0.33333333 +
      2 VCRIT(J)**0.33333333)**3
      TCRIT(J,I)=TCRIT(I,J)
      PCRIT(J,I)=PCRIT(I,J)
100  CONTINUE
110  CONTINUE
      IF (NLIGHT) 200, 200, 120

C
C      READ IN HENRY'S LAW CONSTANTS, PARTIAL MOLAR VOLUMES AT INFINITE
C      DILUTION, AND BINARY INTERACTION PARAMETERS.
C
      120 DO 190 I=1,NLIGHT
      DO 180 J=N1,NCOMP1
      READ(1,905)T1,H1,V1,T2,H2,V2, (CACTCO(I,J,K),CACTCO(J,I,K), K
      1 = 1, NACTCO)
      IF(CACTCO(I,J,1) + CACTCO(J,I,1)) 124,125,124
124  NREFER(I) = J
125  IF(V2) 130,130,140
130  CVLIQL(I,J,2)=(V2-V1)/(T2-T1)
      CVLIQL(I,J,1)=V1-CVLIQL(I,J,2)*T1
      GO TO 150
140  CVLIQL(I,J,2) = (V2-V1)/(T2-T1)
      CVLIQL(I,J,1) = V1-CVLIQL(I,J,2)*T1
150  IF(H2) 160,160,170
160  CHENRY(I,J,2)=0.0
      CHENRY(I,J,1)=H1
      GO TO 180
170  CHENRY(I,J,2) = ALOG(H1/H2)/ALOG(T1/T2)
      CHENRY(I,J,1)=H1/T1*CHENRY(I,J,2)
180  CONTINUE
190  CONTINUE

C
C      READ IN BINARY INTERACTION PARAMETERS FOR COMPONENTS TREATED IN
C      THE SYMMETRIC CONVENTION.
C
      IF (N1 - NCOMP1) 200, 200, 240
200  DO 230 I = N1, NCOMP1
      I1=I+1
      DO 220 J = I1, NCOMP1
      READ(1,905)(CACTCO(I,J,K),CACTCO(J,I,K),K=1,NACTCO)
220  CONTINUE
230  CONTINUE
240  TOLD = 0.0

C
C      SET ALL LIKE-PAIR INTERACTION COEFFICIENTS EQUAL TO ZERO
C
      DO 260 J = 1, NCOMP1
      DO 250 K = 1, NACTCO
      CACTCO(J,J,K) = 0.0

```

```

250 CONTINUE
260 CONTINUE

C
C   READ IN PURE COMPONENT DATA FOR EFFICIENCY CALCULATION
C   :MOLECULAR WEIGHT, LIQUID MOLAL VOLUME AT NORMAL BOILING
C   POINT, BOILING TEMPERATURE, COMPONENT NO. WHOSE
C   EFFICIENCY IS CALCULATED BY DIFFERENCE, CORRECTION TO
C   THE CALCULATED EFFICIENCY, NO. OF COMPONENTS WHOSE
C   EFFICIENCY IS BEING CORRECTED AND THE EFFICIENCY OF
C   THE BOILER
C
READ(1,904)(WM(I),I=1,NCOMP)
READ(1,904)(VO(I),I=1,NCOMP)
READ(1,904)(TB(I),I=1,NCOMP)
READ(1,902) NEF
DO 280 I=1,NCOMP
  VCRT(I) = VCRT(I)
280 CONTINUE
  READ(1,906) IP, IC, NTRAY, ITRAY
  DO 290 I=1,IP
    READ(1,904)(CMP1(I,J),J=1,NCOMP)
290 CONTINUE
    DO 295 I=1,IP
      READ(1,904)(CORF(I,J),J=1,IC)
295 CONTINUE
      FACT(1) = CORF(1,1)*ITRAY+CORF(1,2)
      FACT(2) = CORF(2,1)*(NTRAY-ITRAY)+CORF(2,2)
      DO 320 I=1,IP
        DO 310 J=1,NCOMP
          IF(CMP1(I,J).EQ.0.0) GO TO 300
          DIEF(I,J) = FACT(1)
          GO TO 310
300 DIEF(I,J) = 0.0
310 CONTINUE
320 CONTINUE
      READ(1,904) BFT

901 FORMAT (12A6)
902 FORMAT (3I4)
903 FORMAT (7F8.4,2A6)
904 FORMAT(6F0.0)
905 FORMAT(8F0.0)
906 FORMAT(6I0)
RETURN
END

```

MASTER CHEMICAL

TRAY TO TRAY METHOD OF CALCULATION FOR DISTILLATION
WITH SIMULTANEOUS CHEMICAL REACTION

THIS PROGRAM REQUIRES THE FOLLOWING SUBROUTINES --
NEWTON, GAUSS, BUBLDILFB, EFFICIENCY, INPUTB, RSTATE

PHIMIX, ACTCO, VIRIAL, MODCON, HTCNT, PRINT, WPRINT

```

DIMENSION Z(6), ZF(6), ZX(6), Z1(6)
DIMENSION XN(5), YN(5), ENTF(15), ENTL(15), ENTVR(15)
DIMENSION TITLE(12), EVAPR(15), V(15), BETA(15), ALFA(15)
DIMENSION CODE(12), Q(15), FFD(15), TF(15), FLIQR(15), T(15)
DIMENSION XR(6,15), YR(6,15), XRF(6,15), ENTLR(15)
DIMENSION X11(5), X12(5), X13(5)
DIMENSION CNR(15), ITER(15)
DIMENSION AMT(10,10), BMT(10), YMT(10)
COMMON/TRAY1/ AA(10), BR(10), CC(10), DD(10)
COMMON/TRAY7/ CODE, TITLE
COMMON/TRAY8/ IFIN, NTRAY, ITRAY, NCOMP, TF, T, XR, YR, XRF
COMMON/TRAY9/ FFD, EVAPR, FLIQR, ALFA, BETA, ITER, IS
COMMON/TRAY10/ FLPRO, REFLXR, V, PN
COMMON/TRAY11/ TREF
COMMON/TRAY14/ CNR, Z, ZF, ZX, Z1, X11, DRL1, DRL2
COMMON/FLEET/ IFLG
REAL KL1, KL2
LOGICAL FLF, FLL, FLV, EFFG
CK1(T) = 10.0**(-3.6099-2079.25/T)
CK2(T) = 10.0**(-2.97124+1763.635/T)

```

INITIALIZATION OF THE PROGRAM

```

FLF = .FALSE.
FLL = .FALSE.
FLV = .TRUE.
IFLG = 0
IFIN = 0
IS = 0
READ(1,1999) CODE
READ(1,1999) TITLE
READ(1,2001) IPRINT
1999 FORMAT(12A6)
NPRINT = 0
READ(1,2001) NCOMP, NTRAY, ITRAY, NLIGHT
ITER(NTRAY) = 1
READ(1,2001) M, N
NTRAY1 = NTRAY-1

```



```

READ(1,2002) TREF
READ(1,2002) PN
DO 700 I=1,NTRAY
  READ(1,2002) Q(I)
700 CONTINUE
  READ(1,2002) DRL1, DRL2
  DO 710 I=1,NTRAY
    FFD(I) = 0.0
    TF(I) = 0.0
    ENTF(I) = 0.0
    DO 711 J=1,NCOMP
      XRF(J,I) = 0.0
711 CONTINUE
710 CONTINUE
  DO 730 I=1,NCOMP
    READ(1,2002) AA(I), BB(I), CC(I), DD(I)
730 CONTINUE
    READ(1,2002) FFD(ITRAY), TF(ITRAY)
    READ(1,2002) (XRF(I,ITRAY), I=1,NCOMP)
    READ(1,2002) FLIQR(1), T(1)
    READ(1,2002) (XR(I,1), I=1,NCOMP)
    DO 740 I=2,NTRAY
      FLIQR(I) = FLIQR(1)
      DO 740 J=1,NCOMP
        XR(J,I) = XR(J,1)
740 CONTINUE
    READ(1,2002) RRATIO, PRT, TPRT
    READ(1,2002) ERR, E2
    DELT = (T(1)-TPRT)/NTRAY1
    DO 741 I=1,NTRAY1
      FVAPR(I) = (RRATIO+1.0)*PRT
741 CONTINUE
    TOLD = 0.0
    FLIQR(NTRAY) = RRATIO*PRT
    FVAPR(NTRAY) = 0.0
    DO 744 J=1,NCOMP
      YR(J,NTRAY) = 0.0
744 CONTINUE
    DO 745 I=1,NTRAY
      ALFA(I) = 0.5
      BETA(I) = 0.5
      XX = I
      T(I) = T(1)-(XX-1.0)*DELT
745 CONTINUE
    READ(1,2002) (V(I), I=1,NTRAY)
    DO 746 J=1,NCOMP
      X12(J) = XRF(J,ITRAY)
746 CONTINUE
    IF(FFD(ITRAY).EQ.0.0) GO TO 20
    EFFG = .FALSE.
    CALL BURLDILF(X12, X12, TF(ITRAY), PN, EFFG, ITRAY)
    CALL HTCNT(X12, NCOMP, ENTF(ITRAY), TF(ITRAY), FLV, X13)
20 CONTINUE
    IS = IS + 1
C
C
C
    BOLER STAGE CALCULATION
    DO 30 JJ=1,NCOMP
      X12(JJ) = XR(JJ,1)
30 CONTINUE
    EFFG = .TRUE.
    CALL BURLDILF(X12, YN, T(1), PN, EFFG, 1)
    CALL HTCNT(X12, NCOMP, ENTLR(1), T(1), FLL, X13)
    CALL HTCNT(YN, NCOMP, ENTVR(1), T(1), FLV, X13)
    CALL HTCNT(YN, NCOMP, ENTL(2), T(2), FLL, X11)
    KL1 = CK1(T(2))

```



```

    AMT(2,2) = 1.0
    AMT(2,3) = 1.0
    AMT(3,1) = ENTLR(NTRAY)
    AMT(3,2) = DRL1
    AMT(3,3) = DRL2
    BMT(1) = FVAPR(NTRAY1)*YR(1,NTRAY1)-CK1(T(NTRAY))*FVAPR(NTRAY1)
1 *YR(4,NTRAY1)
    BMT(2) = FVAPR(NTRAY1)
    BMT(3) = FVAPR(NTRAY1)*ENTVR(NTRAY1)-Q(NTRAY)
    CALL GAUSS(3, AMT, BMT, YMT)
    FTOPR = YMT(1)
    ALFA(NTRAY) = YMT(2)
    BETA(NTRAY) = YMT(3)
    FLPRO = FTOPR-FLIQR(NTRAY)
    REFLXR = FLIQR(NTRAY)/FLPRO
    TNEW = 0.0
    DO 90 I=1,NTRAY
    TNEW = TNEW+T(I)
90  CONTINUE
    S = TOLD-TNEW
    TOLD = TNEW

C
C  CONVERGENCE CHECK
C
    IF(ABS(S).LT. ERR) IFIN = 1
    NPRINT = NPRINT+1
    IF(NPRINT.EQ.IPRINT) CALL PRINT
    IF(NPRINT.EQ.IPRINT) NPRINT = 0
    IF(ABS(S).LT. ERR) CALL PRINT
    IF(IFIN.GT. 0) GO TO 100
    GO TO 20

100 STOP
2001 FORMAT(6I0)
2002 FORMAT(10F0.0)
END

```

APPENDIX IX SOLUTION OF PLATE EQUATIONS

The mass balance, energy balance and chemical equilibrium equations for each stage result in a set of nine nonlinear equations in the form of equations IX.1 to IX.9 as introduced in Chapter 4.

$$\begin{aligned} f_1 = & h_1 \cdot LR_{n+1} \cdot XR_{n+1,1} + h_2 \cdot LR_{n+1} \cdot XR_{n+1,2} + h_3 \cdot LR_{n+1,3} \cdot XR_{n+1,3} \\ & + h_4 \cdot LR_{n+1,4} \cdot XR_{n+1,4} + h_5 \cdot LR_{n+1} \cdot XR_{n+1,5} + VR_{n-1} \cdot H_{n-1}^V + F_n \cdot H_n^V \\ & - LR_n \cdot H_n^L - VR_n \cdot H_n^V + Q_n - \alpha_n \cdot L_{n-1} \cdot H_{n-1}^L - \beta_n \cdot L_n \cdot H_n^L = 0 \end{aligned} \quad (IX.1)$$

$$f_2 = XR_{n+1,1} - K_1^L \cdot XR_{n+1,4} = 0 \quad (IX.2)$$

$$f_3 = XR_{n+1,2} - K_2^L \cdot XR_{n+1,1} \cdot XR_{n+1,3} = 0 \quad (IX.3)$$

$$f_4 = XR_{n+1,1} + XR_{n+1,2} + XR_{n+1,3} + XR_{n+1,4} + XR_{n+1,5} - 1 = 0 \quad (IX.4)$$

$$\begin{aligned} f_5 = & LR_{n+1} \cdot XR_{n+1,1} + VR_{n-1} \cdot YR_{n-1,1} + F_n \cdot XF_{n,1} - LR_n \cdot XR_{n,1} - VR_n \cdot YR_{n,1} \\ & - \alpha_n^L \cdot YR_{n,1} - \beta_n^L = 0 \end{aligned} \quad (IX.5)$$

$$\begin{aligned} f_6 = & LR_{n+1} \cdot XR_{n+1,2} + VR_{n-1} \cdot YR_{n-1,2} + F_n \cdot XF_{n,2} - LR_n \cdot XR_{n,2} \\ & - VR_n \cdot YR_{n,2} + \beta_n^L = 0 \end{aligned} \quad (IX.6)$$

$$\begin{aligned} f_7 = & LR_{n+1} \cdot XR_{n+1,3} + VR_{n-1} \cdot YR_{n-1,3} + F_n \cdot XF_{n,3} - LR_n \cdot XR_{n,3} \\ & - VR_n \cdot YR_{n,3} - \beta_n^L = 0 \end{aligned} \quad (IX.7)$$

$$f_8 = LR_{n+1} XR_{n+1,4} + VR_{n-1} YR_{n-1,4} + F_n XF_{n,4} - LR_n XR_{n,4} - VR_n YR_{n,4} + \alpha_n^L = 0 \quad (IX.8)$$

$$f_9 = LR_{n+1} XR_{n+1,5} + VR_{n-1} YR_{n-1,5} + F_n XF_{n,5} - LR_n XR_{n,5} - VR_n YR_{n,5} - \alpha_n^L = 0 \quad (IX.9)$$

The nine variables are $XR_{n+1,1}$, $XR_{n+1,2}$, $XR_{n+1,3}$, $XR_{n+1,4}$, $XR_{n+1,5}$, α_n^L , β_n^L , LR_{n+1} and VR_n , denoted by X_1 to X_9 .

The equations are linearised by the Newton-Raphson method into the form of equation IX.10.

$$A \Delta X = -f \quad (IX.10)$$

where

$$A = \begin{bmatrix} \frac{\partial f_1}{\partial X_1} & \frac{\partial f_1}{\partial X_2} & \dots & \frac{\partial f_1}{\partial X_9} \\ \frac{\partial f_2}{\partial X_1} & \frac{\partial f_2}{\partial X_2} & \dots & \frac{\partial f_2}{\partial X_9} \\ \frac{\partial f_9}{\partial X_1} & \frac{\partial f_9}{\partial X_2} & \dots & \frac{\partial f_9}{\partial X_9} \end{bmatrix} \quad (IX.11)$$

$$\Delta X = \begin{bmatrix} \Delta X_1 \\ \Delta X_2 \\ \cdot \\ \cdot \\ \cdot \\ \Delta X_9 \end{bmatrix} \quad (IX.12)$$

and

$$f = \begin{bmatrix} f_1 \\ f_2 \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ f_9 \end{bmatrix} \quad (IX.13)$$

The solution of equation IX.10 would result in values ΔX_1 to ΔX_9 which are the corrections to the old values of X . The values of X are then updated and matrix A is recalculated resulting in a new form of equation IX.10. The solution is iterated until all the values of ΔX are less than a specified tolerance limit. At this point values of X are taken as the solution of equations IX.1 to IX.9.

APPENDIX X

SPECIFICATION OF MATERIALS

a) Methanol Special for Chromatography

Molecular weight	32.04
Weight per cm ³ at 20°C	0.791 to 0.792 g
Refractive index	1.328 to 1.330
Maximum limits of impurities	
Water	0.025%
Acidity	0.01 ml N%
Non volatile matter	0.0005 %

b) Formaldehyde Solution

Molecular weight	30.03
Weight percent formaldehyde	37 to 41% w
Weight per cm ³	about 1.09 g
Stabilised with about	12% methanol
Impurities less than	0.05%

c) High Purity Helium

Purity not less than	99.9997%
Impurities	
Neon	< 1 Vpm
Nitrogen	< 1 Vpm
Oxygen	< 1 Vpm
Argon	nil
Hydrogen	0.05 Vpm
Carbon dioxide	nil
Water	1 Vpm
Hydrocarbons	< 1 Vpm

APPENDIX XI.1

GAS CHROMATOGRAPH

A PYE 104 series chromatograph with a Katharometer detector head was used for all the analysis. The equipment consisted of the oven, oven temperature controller, the Katharometer power unit, 0. to 1. m.v. recorder and an electronic digital integrator. The columns were 1.5 m long 6 mm diameter stainless steel tubes with PORAPAK T mesh size 80/100. The carrier gas was high purity helium. The samples were injected using a Hamilton high precision, 7001 N syringe with a 70 mm long standard needle. The syringe was equipped with a chaney adaptor for increased repeatability.

The conditions under which the optimum separation was obtained are as follows

a) The carrier gas rate	715. $\text{mm}^3 \cdot \text{s}^{-1}$
b) The inlet pressure of the gas	120.659 kNm^{-2}
c) Oven temperature	135°C
d) Bridge current	150. m.A.
e) Attenuation	50
f) Sample size	1.0 mm^3
g) Formaldehyde retention time	225. s
h) Water retention time	368. s
i) Methanol retention time	425. s

APPENDIX XI.2 CALIBRATION OF GAS CHROMATOGRAPH

The chromatograph was calibrated for water and methanol. Formaldehyde samples were then analysed by the sodium sulphite method for formaldehyde content. The density of samples were then measured. The samples with the known quantity of formaldehyde were analysed on the chromatograph to evaluate the water and methanol content. The formaldehyde weight in the sample was then calculated knowing the total weight of the sample. Samples with known quantity of formaldehyde, methanol and water were then diluted with known quantities of methanol or water for calibration of chromatograph for formaldehyde.

The calibration of the chromatograph for methanol and water was achieved by preparing standard samples of methanol and water. These samples were then injected into the chromatograph and the area of the peaks were plotted against the weight of each component. Therefore knowing the peak area for any unknown sample the weight of the component in the sample could be evaluated using these graphs.

The chromatograph was calibrated for formaldehyde by preparing standard samples of formaldehyde, methanol and water. These samples were then injected into the chromatograph and the area of the peaks for formaldehyde was plotted against the weight of formaldehyde in the sample.

Thus three graphs were obtained, one for each of the components, giving the peak area against the weight of component in the sample. The weight percent of each component could be found with the peak areas for the components.

Since the same syringe was used throughout the experiments and the calibrations, the errors which might have been caused by the error in the syringe are cancelled, therefore minimising the overall error.

The figures XI.1 to XI.3 represent the calibration graphs for the components. Some of the data are listed in Table XI.1.

Table XI.1

Formaldehyde weight (10^{-3} g)	Methanol weight (10^{-3} g)	Water weight (10^{-3} g)	Formaldehyde peak area	Methanol peak area	Water peak area
0.3114	0.1006	0.5888	213	76	500
0.2017	0.5169	0.2810	121	343	201
0.3410	0.1102	0.5497	245	86	461
0.3206	0.2333	0.4466	215	181	350
0.3250	0.2228	0.4527	223	177	358
0.2269	0.0733	0.7004	141	53	609
0.3283	0.2150	0.4573	225	165	370
0.3402	0.1865	0.4746	240	150	384
0.2796	0.0904	0.6307	180	65	538
0.3541	0.1144	0.5324	260	87	438
0.2206	0.0713	0.7087	133	60	615
0.2123	0.0686	0.7197	130	47	641
0.2908	0.0940	0.6159	182	68	524
0.2824	0.3245	0.3933	176	249	303
0.3406	0.1856	0.4745	241	148	382
0.3214	0.2315	0.4477	214	177	359
0.3682	0.1190	0.5129	277	93	422

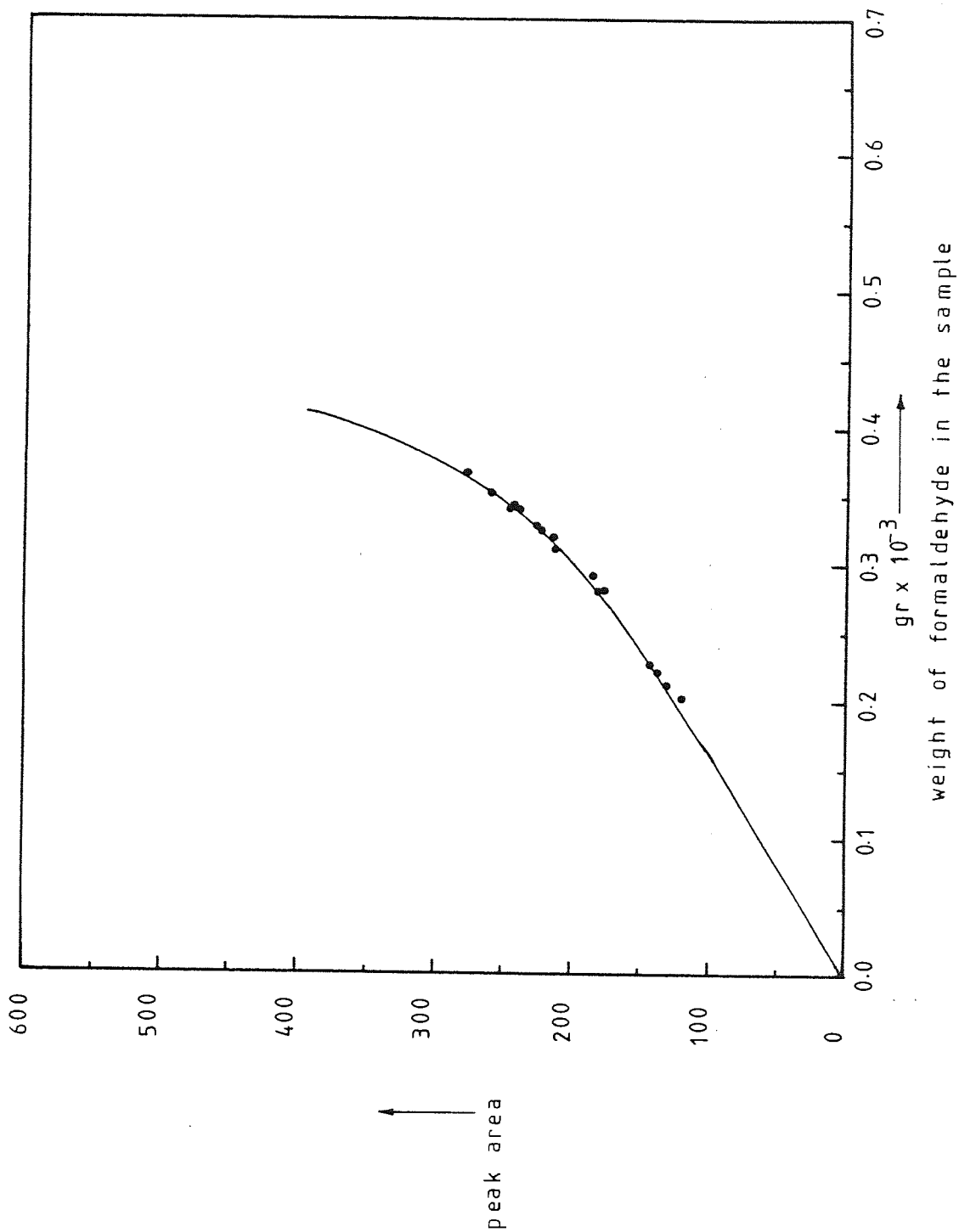


Figure XI.1 calibration of Katharometer for formaldehyde

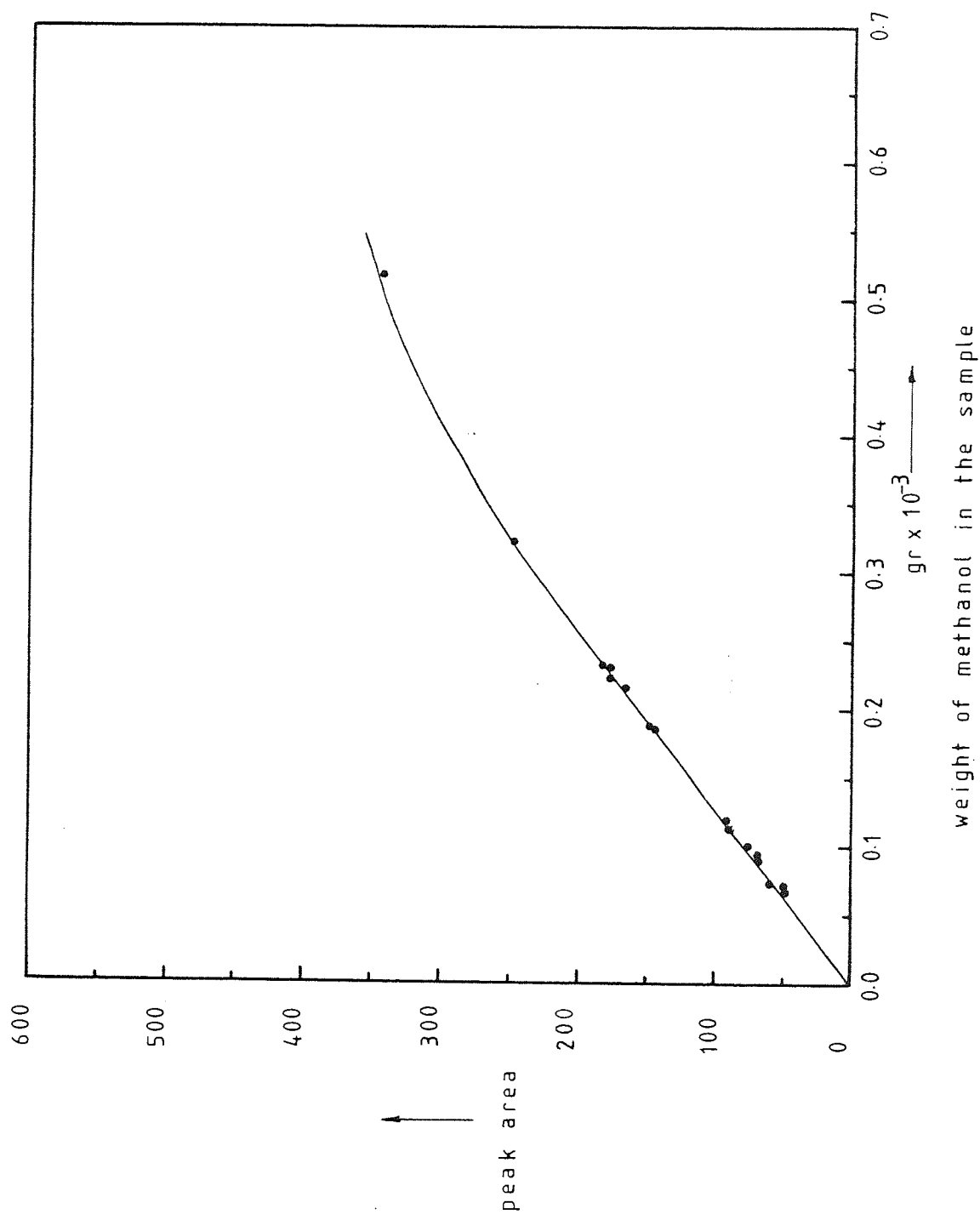


Figure XI.2. calibration of Katharometer for methanol

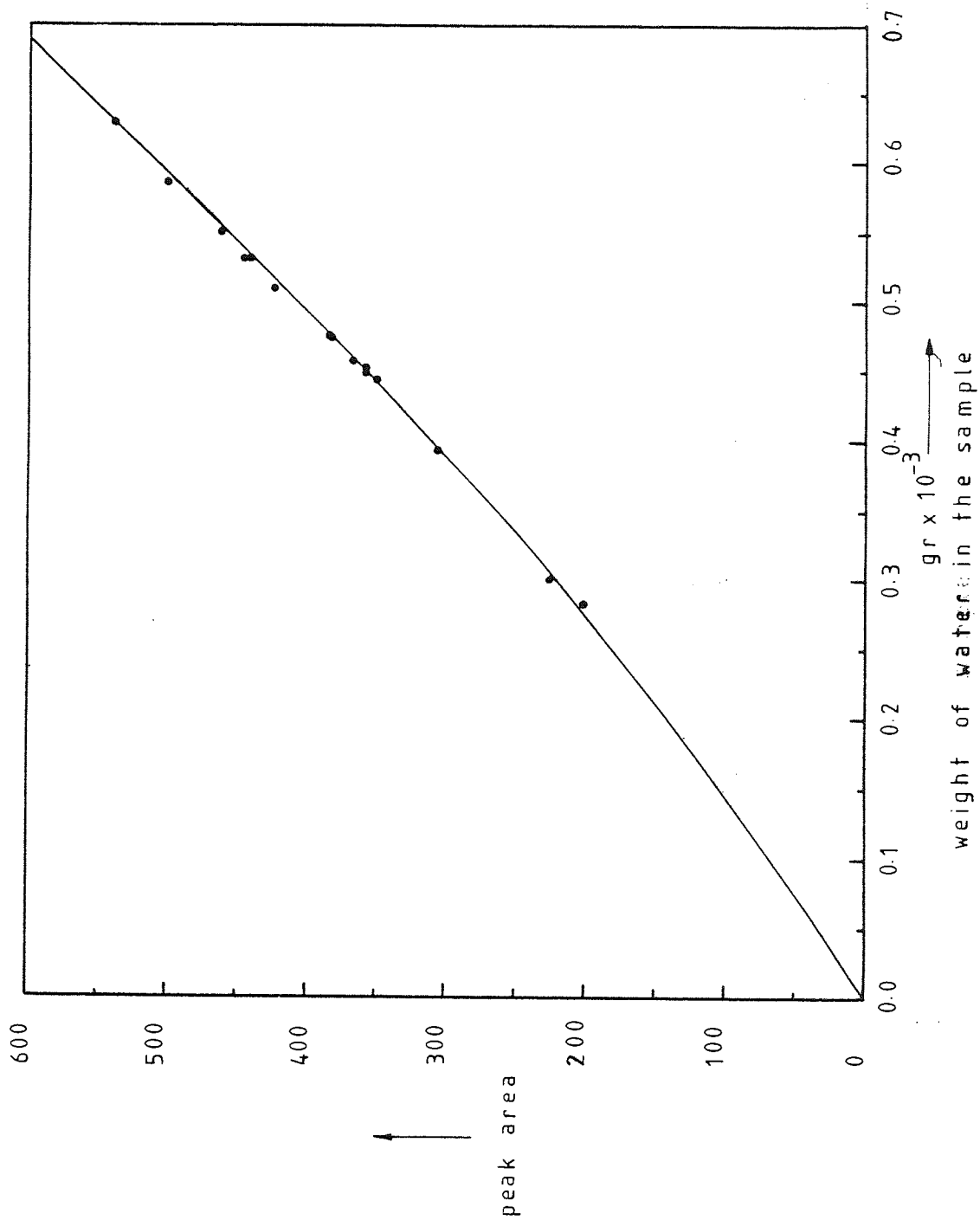


Figure XI.3 calibration of Katharometer for water

APPENDIX XII.1 FORMALDEHYDE-METHYLENE GLYCOL-WATER SYSTEM

The calculated and experimental values for the system of formaldehyde, methylene glycol and water are given in Table XII.1. The experimental data is reported by Olsson and Svensson (73).

APPENDIX XII.2 FORMALDEHYDE-HEMIFORMAL-METHANOL-METHYLENE
GLYCOL-WATER SYSTEM

The calculated and experimental values for the system of formaldehyde, hemiformal, methanol, methylene glycol and water are given in Table XII.2. The experimental data is reported by Walker (41).

APPENDIX XII.3 DISTILLATION EXPERIMENTS

The condition of experiments and specified variables are given in Table XII.3.

APPENDIX XII.4 DISTILLATION RESULTS

The calculated and experimental results for distillation are given in Tables XII.4 to XII.28.

APPENDIX XII.5 PLATE EFFICIENCY VALUES

The actual efficiencies for the experiments are given in Tables XII.29 to XII.53 for the experiments number 1 to 25 respectively. The stages 1 and 10 are the boiler and condenser.

Table XII.1

No.		Mole fraction of formaldehyde	Mole fraction of methylene glycol	Mole fraction of water	T _{EXP} (K)	T _{CAL} (K)
1	X _{EXP}	0.0003	0.0312	0.9684	372.5	372.9
	Y _{EXP}	0.0448	0.0028	0.9524		
	Y _{CAL}	0.0355	0.0021	0.9624		
2	X _{EXP}	0.0005	0.0481	0.9514	372.3	372.8
	Y _{EXP}	0.0631	0.0037	0.9333		
	Y _{CAL}	0.0530	0.0030	0.9440		
3	X _{EXP}	0.0007	0.0659	0.9334	372.1	372.6
	Y _{EXP}	0.0792	0.0037	0.9160		
	Y _{CAL}	0.0703	0.0040	0.9257		
4	X _{EXP}	0.0009	0.0848	0.9144	372.0	372.5
	Y _{EXP}	0.0943	0.0054	0.9003		
	Y _{CAL}	0.0875	0.0049	0.9076		
5	X _{EXP}	0.0013	0.1258	0.8729	371.9	372.3
	Y _{EXP}	0.1212	0.0071	0.8717		
	Y _{CAL}	0.1211	0.0066	0.8723		
6	X _{EXP}	0.0015	0.1482	0.8502	371.9	372.2
	Y _{EXP}	0.1340	0.0077	0.8583		
	Y _{CAL}	0.1377	0.0074	0.8550		
7	X _{EXP}	0.0018	0.1721	0.8261	371.9	372.1
	Y _{EXP}	0.1468	0.0079	0.8453		
	Y _{CAL}	0.1539	0.0081	0.8379		
8	X _{EXP}	0.0021	0.1975	0.8004	371.8	372.0
	Y _{EXP}	0.1587	0.0089	0.8323		
	Y _{CAL}	0.1699	0.0089	0.8212		

Table XII.1 continued

No.		Mole fraction of formaldehyde	Mole fraction of methylene glycol	Mole fraction of water	T _{EXP} (K)	T _{CAL} (K)
9	X _{EXP}	0.0023	0.2247	0.7729	371.8	371.9
	Y _{EXP}	0.1714	0.0090	0.8196		
	Y _{CAL}	0.1857	0.0095	0.8048		
10	X _{EXP}	0.0026	0.2538	0.7436	371.6	371.9
	Y _{EXP}	0.1834	0.0100	0.8066		
	Y _{CAL}	0.2011	0.0101	0.7888		
11	X _{EXP}	0.0030	0.2851	0.7119	371.9	371.8
	Y _{EXP}	0.1965	0.0100	0.7936		
	Y _{CAL}	0.2162	0.0107	0.7731		
12	X _{EXP}	0.0033	0.3187	0.6780	371.9	371.8
	Y _{EXP}	0.2090	0.0110	0.7800		
	Y _{CAL}	0.2310	0.0112	0.7578		
13	X _{EXP}	0.0037	0.3550	0.6413	372.0	371.9
	Y _{EXP}	0.2227	0.0106	0.7664		
	Y _{CAL}	0.2453	0.0116	0.7430		
14	X _{EXP}	0.0041	0.3942	0.6017	372.0	372.0
	Y _{EXP}	0.2362	0.0119	0.7519		
	Y _{CAL}	0.2592	0.0120	0.7288		

Table XII.2

No		Mole fraction of formaldehyde	Mole fraction of hemiformal	Mole fraction of methanol	Mole fraction of methylene glycol	Mole fraction of water	T _{EXP} (K)	T _{CAL} (K)
1	X _{EXP}	0.0003	0.0012	0.0609	0.03177	0.9060		
	Y _{EXP}	0.0152	0.0137	0.2557	0.0010	0.7144	365.6	365.5
	Y _{CAL}	0.0147	0.0133	0.2525	0.0010	0.7185		
2	X _{EXP}	0.0002	0.0024	0.1280	0.0322	0.8372		
	Y _{EXP}	0.0080	0.0163	0.4313	0.0005	0.5438	360.4	360.7
	Y _{CAL}	0.0078	0.0148	0.4032	0.0005	0.5737		
3	X _{EXP}	0.0002	0.0038	0.2023	0.0327	0.7610		
	Y _{EXP}	0.0050	0.0159	0.5475	0.0003	0.4314	356.7	357.1
	Y _{CAL}	0.0047	0.0139	0.5102	0.0003	0.4709		
4	X _{EXP}	0.0002	0.0052	0.2850	0.0333	0.6763		
	Y _{EXP}	0.0029	0.0144	0.6364	0.0002	0.3461	352.1	354.0
	Y _{CAL}	0.0031	0.0126	0.5968	0.0002	0.3873		
5	X _{EXP}	0.0002	0.0070	0.3776	0.0339	0.5814		
	Y _{EXP}	0.0022	0.0139	0.7066	0.0001	0.2773	349.4	351.1
	Y _{CAL}	0.0019	0.0107	0.6749	0.0001	0.3123		

Table XII.2 continued

No		Mole fraction of formaldehyde	Mole fraction of hemiformal	Mole fraction of methanol	Mole fraction of methylene glycol	Mole fraction of water	T _{EXP} (K)	T _{CAL} (K)
6	X _{EXP}	0.0002	0.0089	0.4819	0.0345	0.4745		
	Y _{EXP}	0.0017	0.0139	0.7718	0.0000	0.2125	347.4	348.3
	Y _{CAL}	0.0013	0.0095	0.7474	0.0001	0.2417		
7	X _{EXP}	0.0001	0.0112	0.6003	0.0352	0.3530		
	Y _{EXP}	0.0014	0.0137	0.8366	0.0000	0.1482	345.1	345.5
	Y _{CAL}	0.0009	0.0085	0.8187	0.0000	0.1719		
8	X _{EXP}	0.0001	0.0138	0.7361	0.0361	0.2139		
	Y _{EXP}	0.0011	0.0133	0.8824	0.0000	0.1031	342.3	342.7
	Y _{CAL}	0.0006	0.0075	0.8905	0.0000	0.1013		
9	X _{EXP}	0.0001	0.0169	0.8931	0.0369	0.0530		
	Y _{EXP}	0.0008	0.0129	0.9438	0.0000	0.0424	340.1	339.6
	Y _{CAL}	0.0004	0.0066	0.9642	0.0000	0.0288		
10	X _{EXP}	0.0006	0.0025	0.0631	0.0669	0.8668		
	Y _{EXP}	0.0316	0.0228	0.2200	0.0019	0.7237	366.8	366.1
	Y _{CAL}	0.0331	0.0244	0.2124	0.0021	0.7280		

Table XII.2 continued

No		Mole fraction of formaldehyde	Mole fraction of hemiformal	Mole fraction of methanol	Mole fraction of methylene glycol	Mole fraction of water	T _{EXP} (K)	T _{CAL} (K)
11	X _{EXP}	0.0005	0.0053	0.1331	0.0680	0.7931		
	Y _{EXP}	0.0180	0.0300	0.3880	0.0011	0.5629	361.8	361.5
	Y _{CAL}	0.0181	0.0291	0.3598	0.0012	0.5917		
12	X _{EXP}	0.0004	0.0083	0.2111	0.0692	0.7110		
	Y _{EXP}	0.0106	0.0294	0.5073	0.0007	0.4520	357.6	357.9
	Y _{CAL}	0.0109	0.0285	0.4738	0.0007	0.4861		
13	X _{EXP}	0.0004	0.0118	0.2985	0.0706	0.6188		
	Y _{EXP}	0.0070	0.0287	0.6042	0.0004	0.3597	353.8	354.7
	Y _{CAL}	0.0070	0.0264	0.5705	0.0005	0.3957		
14	X _{EXP}	0.0003	0.0157	0.3970	0.0720	0.5149		
	Y _{EXP}	0.0051	0.0282	0.6758	0.0003	0.2906	350.6	351.7
	Y _{CAL}	0.0043	0.0226	0.6614	0.0003	0.3114		
15	X _{EXP}	0.0003	0.0202	0.5091	0.0736	0.3968		
	Y _{EXP}	0.0038	0.0291	0.7667	0.0002	0.2002	347.8	348.7
	Y _{CAL}	0.0029	0.0202	0.7462	0.0002	0.2306		

Table XII.2 continued

No		Mole fraction of formaldehyde	Mole fraction of hemiformal	Mole fraction of methanol	Mole fraction of methylene glycol	Mole fraction of water	T _{EXP} (K)	T _{CAL} (K)
16	X _{EXP}	0.0003	0.0255	0.6375	0.0752	0.2615		
	Y _{EXP}	0.0030	0.0290	0.8386	0.0001	0.1293	345.5	345.6
	Y _{CAL}	0.0019	0.0180	0.8306	0.0001	0.1494		
17	X _{EXP}	0.0003	0.0316	0.7864	0.0772	0.1046		
	Y _{EXP}	0.0023	0.0284	0.8900	0.0000	0.0793	342.2	342.3
	Y _{CAL}	0.0012	0.0158	0.9168	0.0000	0.0661		
18	X _{EXP}	0.0014	0.0062	0.0681	0.1509	0.7735		
	Y _{EXP}	0.0766	0.0443	0.1942	0.0039	0.6809	368.2	367.3
	Y _{CAL}	0.0814	0.0376	0.1426	0.0049	0.7335		
19	X _{EXP}	0.0012	0.0132	0.1445	0.1538	0.6873		
	Y _{EXP}	0.0523	0.0570	0.3026	0.0028	0.5855	364.5	363.3
	Y _{CAL}	0.0486	0.0537	0.2738	0.0031	0.6209		
20	X _{EXP}	0.0011	0.0210	0.2310	0.1572	0.5897		
	Y _{EXP}	0.0321	0.0615	0.4176	0.0018	0.4870	360.1	359.8
	Y _{CAL}	0.0296	0.0581	0.3979	0.0019	0.5125		

Table XII.2 continued

No		Mole fraction of formaldehyde	Mole fraction of hemiformal	Mole fraction of methanol	Mole fraction of methylene glycol	Mole fraction of water	T _{EXP} (K)	T _{CAL} (K)
21	X _{EXP}	0.0010	0.0300	0.3296	0.1608	0.4786		
	Y _{EXP}	0.0211	0.0634	0.5333	0.0011	0.3810	356.5	356.3
	Y _{CAL}	0.0184	0.0571	0.5176	0.0011	0.4058		
22	X _{EXP}	0.0009	0.0406	0.4429	0.1648	0.3508		
	Y _{EXP}	0.0152	0.0638	0.6106	0.0008	0.3096	353.1	353.0
	Y _{CAL}	0.0108	0.0507	0.6428	0.0006	0.2952		
23	X _{EXP}	0.0008	0.0529	0.5745	0.1694	0.2024		
	Y _{EXP}	0.0108	0.0693	0.7542	0.0004	0.1654	349.4	349.4
	Y _{CAL}	0.0066	0.0461	0.7649	0.0003	0.1821		
24	X _{EXP}	0.0025	0.0116	0.0739	0.2595	0.6525		
	Y _{EXP}	0.1217	0.0445	0.1280	0.0061	0.6996	369.0	368.7
	Y _{CAL}	0.1425	0.0386	0.0902	0.0078	0.7209		
25	X _{EXP}	0.0023	0.0251	0.1581	0.2658	0.5487		
	Y _{EXP}	0.0941	0.0724	0.2377	0.0045	0.5913	366.2	365.6
	Y _{CAL}	0.0954	0.0673	0.1977	0.0054	0.6342		

Table XII.2 continued

No		Mole fraction of formaldehyde	Mole fraction of hemiformal	Mole fraction of methanol	Mole fraction of methylene glycol	Mole fraction of water	T _{EXP} (K)	T _{CAL} (K)
26	X _{EXP}	0.0021	0.0409	0.2552	0.2729	0.4290		
	Y _{EXP}	0.0708	0.0882	0.3252	0.0035	0.5123	362.9	362.4
	Y _{CAL}	0.0605	0.0846	0.3271	0.0034	0.5243		
27	X _{EXP}	0.0019	0.0595	0.3683	0.2809	0.2895		
	Y _{EXP}	0.0491	0.1026	0.4463	0.0023	0.3998	359.1	358.8
	Y _{CAL}	0.0365	0.0918	0.4807	0.0019	0.3891		
28	X _{EXP}	0.0040	0.0200	0.0807	0.4058	0.4895		
	Y _{EXP}	0.1645	0.0515	0.1172	0.0073	0.6595	370.1	370.7
	Y _{CAL}	0.2095	0.0312	0.0550	0.0099	0.6943		
29	X _{EXP}	0.0037	0.0440	0.1747	0.4188	0.3588		
	Y _{EXP}	0.1393	0.0796	0.1876	0.0063	0.5872	367.2	369.0
	Y _{CAL}	0.1578	0.0676	0.1444	0.0073	0.6229		
30	X _{EXP}	0.0060	0.0157	0.0427	0.6019	0.3336		
	Y _{EXP}	0.2324	0.0373	0.0607	0.0102	0.6594	370.6	374.0
	Y _{CAL}	0.2921	0.0091	0.0137	0.0112	0.6739		

Table XII.3

Experiment number	Reflux ratio	Feed concentration			Feed rate g/s	Feed stage	Feed temperature (°C)	Heat input kJ/s	Heat output kJ/s	Laboratory pressure (kNm ⁻²)	Laboratory temperature (°C)
		X _{form}	X _{meth}	X _{water}							
1	10	0.2802	0.1763	0.5435	0.257	8	98.8	1.041	0.396	100.271	25.0
2	10	0.3355	0.0674	0.5971	0.119	8	97.9	1.199	0.555	100.271	22.0
3	10	0.3148	0.0895	0.5957	0.271	8	91.9	1.189	0.504	100.291	24.0
4	10	0.3274	0.0824	0.5902	0.407	8	91.0	1.304	0.728	100.170	24.0
5	15	0.2921	0.0755	0.6324	0.398	8	91.0	1.738	0.938	100.474	22.5
6	total	-	-	-	-	-	-	2.076	1.242	98.650	22.0
7	20	0.3065	0.0927	0.6008	0.355	8	92.0	1.064	0.349	97.698	21.0
8	10	0.3030	0.0205	0.6765	0.433	8	97.3	2.097	1.209	98.984	23.0
9	5	0.3054	0.0345	0.6601	0.397	8	96.0	1.990	1.241	99.116	22.5
10	total	-	-	-	-	-	-	1.234	0.621	98.630	20.0
11	20	0.3029	0.0258	0.6713	0.404	7	96.3	2.079	0.393	99.076	21.0
12	10	0.3557	0.1243	0.5200	0.357	7	97.0	1.420	0.842	97.191	20.0
13	5	0.3065	0.0251	0.6684	0.432	7	94.5	2.540	1.548	99.147	19.0
14	total	-	-	-	-	-	-	1.400	0.884	99.045	21.0
15	20	0.3537	0.1063	0.5399	0.362	6	89.5	1.469	0.872	97.890	20.0

Table XII.3 continued

Experiment number	Reflux ratio	Feed concentration weight fraction			Feed rate g/s	Feed stage	Feed temperature (°C)	Heat input kJ/s	Heat output kJ/s	Laboratory pressure (kNm ⁻²)	Laboratory temperature (°C)
		X _{form}	X _{meth}	X _{water}							
16	10	0.3690	0.0645	0.5666	0.425	6	96.5	1.312	0.629	97.353	20.0
17	5	0.3726	0.0624	0.5650	0.393	6	94.5	1.485	0.794	99.116	20.0
18	20	0.3608	0.0884	0.5508	0.377	5	95.3	2.140	1.945	101.153	21.0
19	10	0.3617	0.0836	0.5547	0.410	5	93.3	2.043	1.884	100.788	22.0
20	5	0.3683	0.0709	0.5608	0.424	5	96.8	2.081	1.468	100.879	24.0
21	total	-	-	-	-	-	-	1.808	1.109	99.856	20.0
22	20	0.3629	0.0792	0.5579	0.400	4	95.8	2.119	1.476	98.407	19.0
23	10	0.3675	0.0583	0.5742	0.383	4	96.8	2.031	1.377	99.471	19.0
24	5	0.3760	0.0501	0.5740	0.362	4	96.7	2.048	1.221	99.795	20.0
25	total	-	-	-	-	-	-	2.140	1.350	99.329	19.0

Table XII.4 Experiment 1

Stage No.	Experimental formaldehyde wt fraction	Experimental methanol wt fraction	Experimental water wt fraction	Calculated formaldehyde wt fraction	Calculated methanol wt fraction	Calculated water wt fraction	T _{exp} (°C)	T _{cal} (°C)
1	0.3361	0.0552	0.6087	0.3361	0.0552	0.6087	97.0	100.5
2	0.2943	0.1220	0.5837	0.2979	0.0883	0.6138	96.5	99.1
3	0.2967	0.1303	0.5730	0.2862	0.1062	0.6077	96.0	98.3
4	0.2926	0.1526	0.5547	0.2679	0.1224	0.6097	95.6	97.5
5	0.2962	0.1559	0.5479	0.2591	0.1380	0.6029	95.1	96.8
6	0.2904	0.1476	0.5620	0.2459	0.1505	0.6039	94.7	96.1
7	0.3121	0.1627	0.5252	0.2312	0.1611	0.6077	95.0	95.5
8	0.2908	0.1442	0.5650	0.2182	0.1698	0.6119	73.0	94.9
9				0.1538	0.3609	0.4853	87.0	83.9
10	0.0597	0.6994	0.2409	0.0582	0.6367	0.3051	74.0	74.4

Table XII.5 Experiment 2

Stage No.	Experimental formaldehyde wt fraction	Experimental methanol wt fraction	Experimental water wt fraction	Calculated formaldehyde wt fraction	Calculated methanol wt fraction	Calculated water wt fraction	T _{exp} (°C)	T _{cal} (°C)
1	0.3355	0.0674	0.5971	0.3365	0.0539	0.6095	99.0	100.5
2	0.3084	0.0942	0.5973	0.2988	0.0862	0.6150	98.8	99.2
3	0.3073	0.0910	0.6017	0.2823	0.1092	0.6085	98.5	98.2
4	0.3054	0.1129	0.5816	0.2625	0.1304	0.6071	98.0	97.1
5	0.3009	0.1205	0.5786	0.2537	0.1508	0.5955	97.0	96.3
6	0.2882	0.1580	0.5538	0.2408	0.1668	0.5924	95.0	92.4
7	0.2585	0.2228	0.5187	0.2372	0.1759	0.5869	93.0	92.0
8	0.2167	0.3109	0.4724	0.2387	0.1866	0.5747	87.0	91.7
9				0.1753	0.3883	0.4364	76.8	83.3
10	0.0364	0.7955	0.1682	0.0635	0.6486	0.2879	68.9	74.1

Table XII.6 Experiment 3

Stage No.	Experimental formaldehyde wt fraction	Experimental methanol wt fraction	Experimental water wt fraction	Calculated formaldehyde wt fraction	Calculated methanol wt fraction	Calculated water wt fraction	T _{exp} (°C)	T _{cal} (°C)
1	0.3414	0.0205	0.6381	0.3414	0.0205	0.6381	98.8	101.4
2	0.3207	0.0692	0.6101	0.3156	0.0355	0.6489	98.3	100.8
3	0.3233	0.0865	0.5902	0.3270	0.0511	0.6219	97.9	100.5
4	0.3289	0.0779	0.5932	0.3232	0.0665	0.6103	97.0	100.1
5	0.3193	0.1159	0.5648	0.3196	0.0815	0.5990	96.3	99.6
6	0.3071	0.1533	0.5395	0.3075	0.0954	0.5971	95.0	99.0
7	0.2925	0.1941	0.5134	0.2941	0.1086	0.5973	94.0	98.4
8	0.2533	0.2214	0.5252	0.2818	0.1211	0.5971	91.8	97.8
9				0.0318	0.3298	0.6384	82.1	82.9
10	0.0195	0.8113	0.1692	0.0089	0.6660	0.3252	70.0	73.5

Table XII.7 Experiment 4

Stage No.	Experimental formaldehyde wt fraction	Experimental methanol wt fraction	Experimental water wt fraction	Calculated formaldehyde wt fraction	Calculated methanol wt fraction	Calculated water wt fraction	T _{exp} (°C)	T _{cal} (°C)
1	0.3460	0.0389	0.6151	0.3458	0.0388	0.6153	98.3	100.9
2	0.3166	0.0775	0.6059	0.3222	0.0567	0.6211	98.0	100.3
3	0.3268	0.0798	0.5934	0.3181	0.0715	0.6104	97.2	99.9
4	0.3099	0.1060	0.5842	0.3048	0.0851	0.6102	96.5	99.3
5	0.2894	0.1061	0.6045	0.2997	0.0980	0.6023	96.0	98.8
6	0.2932	0.1359	0.5709	0.2901	0.1093	0.6007	95.0	98.3
7	0.2864	0.1689	0.5446	0.2788	0.1196	0.6016	94.5	97.8
8	0.2778	0.1906	0.5316	0.2687	0.1290	0.6023	93.0	97.3
9				0.0531	0.3507	0.5961	84.5	82.6
10	0.0639	0.7087	0.2275	0.0133	0.6743	0.3124	70.0	73.3

Table XII.8 Experiment 5

Stage No.	Experimental formaldehyde wt fraction	Experimental methanol wt fraction	Experimental water wt fraction	Calculated formaldehyde wt fraction	Calculated methanol wt fraction	Calculated water wt fraction	T _{exp} (°C)	T _{cal} (°C)
1	0.3130	0.0122	0.6748	0.3130	0.0122	0.6748	99.3	98.5
2	0.3022	0.0253	0.6725	0.3119	0.0145	0.6736	98.6	101.4
3	0.3093	0.0373	0.6534	0.3074	0.0344	0.6582	98.4	100.8
4	0.3071	0.0555	0.6375	0.2876	0.0593	0.6531	98.0	99.9
5	0.3175	0.0683	0.6143	0.2697	0.0880	0.6423	97.8	98.7
6	0.2999	0.0907	0.6094	0.2465	0.1186	0.6349	96.8	97.3
7	0.2963	0.1137	0.5900	0.2219	0.1501	0.6280	96.8	95.7
8	0.2926	0.1521	0.5553	0.1994	0.1807	0.6198	94.8	91.1
9				0.1273	0.3781	0.4946	90.5	83.8
10	0.1346	0.5237	0.3416	0.0611	0.6153	0.3235	70.5	75.0

Table XII.9 Experiment 6

Stage No.	Experimental formaldehyde wt fraction	Experimental methanol wt fraction	Experimental water wt fraction	Calculated formaldehyde wt fraction	Calculated methanol wt fraction	Calculated water wt fraction	T _{exp} (°C)	T _{cal} (°C)
1	0.2974	0.0084	0.6942	0.2974	0.0084	0.6942	99.8	93.6
2	0.3002	0.0010	0.6988	0.2976	0.0112	0.6911	99.3	93.5
3	0.2816	0.0001	0.7175	0.2979	0.0187	0.6834	99.0	101.3
4	0.2945	0.0037	0.7018	0.2838	0.0555	0.6607	99.8	99.9
5	0.2747	0.0112	0.7141	0.2561	0.1162	0.6277	98.6	97.5
6	0.2796	0.0266	0.6939	0.2144	0.1919	0.5936	97.5	91.0
7	0.2802	0.0716	0.6482	0.1846	0.2596	0.5557	96.3	87.9
8	0.2677	0.1544	0.5779	0.1758	0.3235	0.5007	92.6	85.5
9				0.1670	0.3770	0.4560	85.0	83.6
10	0.1198	0.4388	0.4414	0.1541	0.4214	0.4246	71.3	81.9

Table XII.10 Experiment 7

Stage No.	Experimental formaldehyde wt fraction	Experimental methanol wt fraction	Experimental water wt fraction	Calculated formaldehyde wt fraction	Calculated methanol wt fraction	Calculated water wt fraction	T _{exp} (°C)	T _{cal} (°C)
1	0.3021	0.0904	0.6075	0.3021	0.0904	0.6076	97.7	99.1
2	0.2431	0.1054	0.6515	0.2727	0.1230	0.6042	96.3	97.6
3	0.2996	0.1377	0.5628	0.2598	0.1359	0.6042	95.3	96.9
4	0.2904	0.1682	0.5414	0.2457	0.1468	0.6075	94.3	96.2
5	0.2918	0.1595	0.5487	0.2378	0.1569	0.6053	93.8	95.7
6	0.2891	0.1716	0.5425	0.2277	0.1641	0.6082	93.3	95.3
7	0.2863	0.1671	0.5466	0.2168	0.1696	0.6136	93.8	91.8
8	0.2838	0.1572	0.5590	0.2178	0.1756	0.6066	93.3	91.6
9				0.1571	0.3899	0.4530	84.0	83.0
10	0.1622	0.5885	0.2494	0.0526	0.6590	0.2884	63.8	73.8

Table XII.11 Experiment 8

Stage No.	Experimental formaldehyde wt fraction	Experimental methanol wt fraction	Experimental water wt fraction	Calculated formaldehyde wt fraction	Calculated methanol wt fraction	Calculated water wt fraction	T _{exp} (°C)	T _{cal} (°C)
1	0.3025	0.0025	0.6951	0.3025	0.0024	0.6951	98.9	98.8
2	0.2980	0.0062	0.6958	0.3050	0.0040	0.6910	98.7	98.7
3	0.2946	0.0074	0.6980	0.3056	0.0060	0.6885	98.6	98.7
4	0.2931	0.0111	0.6958	0.3056	0.0085	0.6859	98.2	98.6
5	0.2917	0.0136	0.6948	0.3056	0.0116	0.6832	98.0	98.5
6	0.2915	0.0178	0.6906	0.3040	0.0156	0.6804	97.5	101.4
7	0.2976	0.0323	0.6691	0.2696	0.0450	0.6855	97.4	100.3
8	0.3021	0.0666	0.6313	0.2197	0.0989	0.6814	95.75	97.7
9				0.1177	0.2465	0.6358	93.0	87.1
10	0.2407	0.2417	0.5176	0.0778	0.4164	0.5059	82.5	80.9

Table XII.12 Experiment 9

Stage No.	Experimental formaldehyde wt fraction	Experimental methanol wt fraction	Experimental water wt fraction	Calculated formaldehyde wt fraction	Calculated methanol wt fraction	Calculated water wt fraction	T _{exp} (°C)	T _{cal} (°C)
1	0.3145	0.0010	0.6846	0.3115	0.0070	0.6816	99.5	98.7
2	0.3027	0.0010	0.6964	0.3108	0.0109	0.6784	99.25	98.5
3	0.2990	0.0025	0.6985	0.3110	0.0128	0.6762	99.0	98.5
4	0.2998	0.0084	0.6918	0.3128	0.0149	0.6723	98.6	101.4
5	0.2986	0.0131	0.6883	0.3233	0.0275	0.6491	98.4	101.1
6	0.2984	0.0345	0.6672	0.3234	0.0420	0.6346	97.75	100.7
7	0.2994	0.0514	0.6492	0.3344	0.0565	0.6091	97.5	100.4
8	0.2356	0.0869	0.6774	0.3358	0.0707	0.5935	95.5	100.1
9				0.3083	0.1660	0.5257	94.25	93.9
10	0.2066	0.3390	0.4544	0.2466	0.2458	0.5076	79.0	89.8

Table XII.13 Experiment 10

Stage No.	Experimental formaldehyde wt fraction	Experimental methanol wt fraction	Experimental water wt fraction	Calculated formaldehyde wt fraction	Calculated methanol wt fraction	Calculated water wt fraction	T _{exp} (°C)	T _{cal} (°C)
1	0.3090	0.0224	0.6686	0.3090	0.0224	0.6686	98.5	101.2
2	0.2961	0.0434	0.6606	0.2724	0.0462	0.6815	97.8	100.2
3	0.2985	0.0519	0.6496	0.2210	0.1050	0.6740	97.3	97.4
4	0.2924	0.0902	0.6174	0.1582	0.1871	0.6546	96.3	90.1
5	0.2861	0.1408	0.5732	0.1305	0.2720	0.5976	95.3	86.5
6	0.2658	0.2028	0.5314	0.1192	0.3438	0.5370	92.8	83.8
7	0.1949	0.3570	0.4482	0.1063	0.3996	0.4942	88.5	81.9
8	0.1055	0.6070	0.2876	0.0941	0.4456	0.4603	80.3	80.3
9				0.0899	0.4847	0.4253	70.0	79.1
10	0.0494	0.7738	0.1768	0.0774	0.5143	0.4083	61.8	78.1

Table XII.14 Experiment 11

Stage No.	Experimental formaldehyde wt fraction	Experimental methanol wt fraction	Experimental water wt fraction	Calculated formaldehyde wt fraction	Calculated methanol wt fraction	Calculated water wt fraction	T _{exp} (°C)	T _{cal} (°C)
1	0.3070	0.0010	0.6920	0.3062	0.0026	0.6912	101.8	98.8
2	0.2995	0.0010	0.6995	0.3069	0.0031	0.6900	101.3	98.8
3	0.3008	0.0060	0.6933	0.3078	0.0048	0.6874	101.3	98.7
4	0.3068	0.0074	0.6858	0.3081	0.0070	0.6849	101.0	98.6
5	0.3031	0.0179	0.6789	0.3081	0.0097	0.6822	100.5	98.6
6	0.2964	0.0435	0.6602	0.3075	0.0131	0.6795	99.6	98.5
7	0.2836	0.0662	0.6502	0.3059	0.0173	0.6768	99.5	101.3
8	0.2857	0.1542	0.5601	0.2117	0.0802	0.7082	96.5	98.4
9	0.2417	0.3142	0.4442	0.0727	0.2716	0.6557	91.3	85.5
10	0.1201	0.5525	0.3274	0.0356	0.5657	0.3987	75.0	76.3

Table XII.15 Experiment 12

Stage No.	Experimental formaldehyde wt fraction	Experimental methanol wt fraction	Experimental water wt fraction	Calculated formaldehyde wt fraction	Calculated methanol wt fraction	Calculated water wt fraction	T _{exp} (°C)	T _{cal} (°C)
1	0.3642	0.0755	0.5604	0.3642	0.0755	0.5604	97.8	100.4
2	0.3455	0.0829	0.5716	0.3302	0.1040	0.5658	96.8	99.2
3	0.3401	0.0999	0.5599	0.3143	0.1194	0.5664	96.0	98.4
4	0.3296	0.1341	0.5364	0.2987	0.1330	0.5683	95.0	97.7
5	0.3193	0.1589	0.5217	0.2910	0.1458	0.5632	94.3	97.2
6	0.3108	0.1955	0.4937	0.2792	0.1561	0.5647	93.0	96.6
7	0.2942	0.2297	0.4761	0.2665	0.1648	0.5687	92.4	93.0
8	0.1934	0.4132	0.3934	0.1900	0.3020	0.5080	84.3	86.6
9				0.1001	0.5221	0.3777	73.3	78.1
10	0.0046	0.9148	0.0807	0.0383	0.7225	0.2392	65.0	72.0

Table XII.16 Experiment 13

Stage No.	Experimental formaldehyde wt fraction	Experimental methanol wt fraction	Experimental water wt fraction	Calculated formaldehyde wt fraction	Calculated methanol wt fraction	Calculated water wt fraction	T _{exp} (°C)	T _{cal} (°C)
1	0.3172	0.0010	0.6818	0.3165	0.0024	0.6811	100.0	48.8
2	0.3058	0.0010	0.6938	0.3167	0.0029	0.6804	99.5	98.8
3	0.3005	0.0010	0.6985	0.3170	0.0046	0.6784	99.3	98.7
4	0.3015	0.0010	0.6975	0.3171	0.0069	0.6759	99.1	98.6
5	0.3019	0.0010	0.6971	0.3169	0.0101	0.6730	99.0	98.6
6	0.2981	0.0120	0.6895	0.3158	0.0144	0.6698	98.4	101.4
7	0.2975	0.0240	0.6788	0.2830	0.0470	0.6700	98.6	100.3
8	0.2963	0.0440	0.6595	0.1538	0.1754	0.6708	97.0	90.5
9	0.2822	0.1083	0.6095	0.0987	0.4179	0.4834	94.5	81.2
10	0.2581	0.1985	0.5434	0.0435	0.6626	0.2939	85.0	73.6

Table XII.17 Experiment 14

Stage No.	Experimental formaldehyde wt fraction	Experimental methanol wt fraction	Experimental water wt fraction	Calculated formaldehyde wt fraction	Calculated methanol wt fraction	Calculated water wt fraction	T _{exp} (°C)	T _{cal} (°C)
1	0.3695	0.0501	0.5804	0.3695	0.0501	0.5804	98.5	101.0
2	0.3319	0.0630	0.6051	0.3207	0.0872	0.5921	97.0	99.5
3	0.3249	0.0772	0.5979	0.1802	0.1996	0.6202	96.8	90.0
4	0.2987	0.1301	0.5712	0.1140	0.3403	0.5457	95.3	83.8
5	0.2820	0.1853	0.5327	0.0859	0.4949	0.4193	92.4	78.7
6	0.1989	0.3591	0.4420	0.0571	0.6086	0.3342	85.0	75.2
7	0.0606	0.7396	0.1998	0.0324	0.6903	0.2772	75.0	72.9
8	0.0019	0.9230	0.0751	0.0133	0.7517	0.2350	68.5	71.2
9	0.0019	0.9535	0.0446	0.0042	0.7966	0.1991	64.8	70.0
10	0.0010	0.9501	0.0489	0.0011	0.8311	0.1678	60.5	69.1

Table XII.18 Experiment 15

Stage No.	Experimental formaldehyde wt fraction	Experimental methanol wt fraction	Experimental water wt fraction	Calculated formaldehyde wt fraction	Calculated methanol wt fraction	Calculated water wt fraction	T _{exp} (°C)	T _{cal} (°C)
1	0.3773	0.0337	0.5890	0.3773	0.0337	0.5890	98.8	101.3
2	0.3478	0.0547	0.5975	0.3515	0.0511	0.5974	97.0	100.8
3	0.3466	0.0718	0.5817	0.3412	0.0673	0.5915	96.5	100.3
4	0.3361	0.1029	0.5610	0.3283	0.0823	0.5894	96.0	99.7
5	0.3284	0.1293	0.5422	0.3235	0.0966	0.5799	95.5	99.2
6	0.3247	0.1546	0.5206	0.3124	0.1092	0.5783	93.8	98.7
7	0.2724	0.2449	0.4827	0.1161	0.2491	0.6348	90.3	83.0
8	0.1522	0.4895	0.3583	0.0641	0.4798	0.4561	80.5	78.9
9	0.0340	0.8192	0.1468	0.0357	0.6686	0.2957	70.8	73.5
10	0.0017	0.9480	0.0502	0.0141	0.7876	0.1983	64.5	70.2

Table XII.19 Experiment 16

Stage No.	Experimental formaldehyde wt fraction	Experimental methanol wt fraction	Experimental water wt fraction	Calculated formaldehyde wt fraction	Calculated methanol wt fraction	Calculated water wt fraction	T _{exp} (°C)	T _{cal} (°C)
1	0.3725	0.0402	0.5874	0.3725	0.0402	0.5874	98.5	101.2
2	0.3517	0.0589	0.5894	0.3313	0.0696	0.5991	97.3	100.1
3	0.3437	0.0772	0.5791	0.3279	0.0769	0.5952	96.8	99.8
4	0.3424	0.0780	0.5796	0.3227	0.0832	0.5941	96.3	99.6
5	0.3418	0.0994	0.5589	0.3250	0.0890	0.5860	96.0	99.5
6	0.3472	0.0946	0.5582	0.3232	0.0936	0.5832	94.5	99.3
7	0.2762	0.2425	0.4813	0.1892	0.1908	0.6200	92.0	90.5
8	0.2696	0.2533	0.4771	0.1416	0.3092	0.5492	86.4	85.4
9	0.1825	0.5138	0.3037	0.1103	0.4291	0.4606	75.2	81.0
10	0.0467	0.7992	0.1541	0.0821	0.5310	0.3869	67.0	77.6

Table XII.20 Experiment 17

Stage No.	Experimental formaldehyde wt fraction	Experimental methanol wt fraction	Experimental water wt fraction	Calculated formaldehyde wt fraction	Calculated methanol wt fraction	Calculated water wt fraction	T _{exp} (°C)	T _{cal} (°C)
1	0.3871	0.0115	0.6014	0.3871	0.0115	0.6014	99.8	98.8
2	0.3612	0.0215	0.6173	0.3826	0.0119	0.6055	98.7	98.7
3	0.3563	0.0339	0.6098	0.3825	0.0126	0.6049	98.6	98.7
4	0.3544	0.0503	0.5953	0.3812	0.0132	0.6057	98.2	98.7
5	0.3533	0.0513	0.5955	0.3807	0.0137	0.6056	98.0	101.7
6	0.3496	0.0653	0.5851	0.3713	0.0368	0.5919	97.3	101.2
7	0.3304	0.0764	0.5932	0.2816	0.0779	0.6404	97.0	99.2
8	0.3053	0.1476	0.5471	0.2024	0.1525	0.6451	95.0	85.3
9	0.2588	0.2498	0.4914	0.1219	0.2626	0.6155	91.3	76.6
10	0.1477	0.4830	0.3693	0.0838	0.3740	0.5422	76.3	72.3

Table XII.21 Experiment 18

Stage No.	Experimental formaldehyde wt fraction	Experimental methanol wt fraction	Experimental water wt fraction	Calculated formaldehyde wt fraction	Calculated methanol wt fraction	Calculated water wt fraction	T _{exp} (°C)	T _{cal} (°C)
1	0.3973	0.0010	0.6016	0.3933	0.0090	0.5976	100.8	98.8
2	0.3694	0.0090	0.6216	0.3760	0.0099	0.6141	99.5	98.7
3	0.3669	0.0146	0.6217	0.3661	0.0123	0.6216	99.25	98.6
4	0.3573	0.0267	0.6159	0.3599	0.0157	0.6244	99.0	101.4
5	0.3545	0.0385	0.6069	0.2841	0.0757	0.6401	98.8	99.3
6	0.3426	0.0510	0.6065	0.2582	0.0837	0.6581	98.0	98.7
7	0.3344	0.0734	0.5922	0.2658	0.0961	0.6381	97.8	98.4
8	0.3167	0.1252	0.5581	0.2742	0.1054	0.6204	96.0	98.1
9	0.2864	0.2194	0.4942	0.2907	0.1128	0.5965	92.8	98.2
10	0.2120	0.3501	0.4380	0.3029	0.1204	0.5767	78.0	98.2

Table XII.22 Experiment 19

Stage No.	Experimental formaldehyde wt fraction	Experimental methanol wt fraction	Experimental water wt fraction	Calculated formaldehyde wt fraction	Calculated methanol wt fraction	Calculated water wt fraction	T _{exp} (°C)	T _{cal} (°C)
1	0.3972	0.0010	0.6017	0.3932	0.0090	0.5977	100.0	98.8
2	0.3647	0.0088	0.6264	0.3772	0.0098	0.6129	99.5	98.7
3	0.3604	0.0203	0.6193	0.3685	0.0119	0.6196	99.0	98.7
4	0.3553	0.0265	0.6182	0.3637	0.0145	0.6218	98.8	101.6
5	0.3534	0.0382	0.6085	0.2908	0.0687	0.6405	98.6	99.6
6	0.3387	0.0473	0.6140	0.2620	0.0742	0.6638	98.2	99.1
7	0.3227	0.0710	0.6063	0.2670	0.0866	0.6464	98.0	98.7
8	0.3150	0.1136	0.5715	0.2792	0.0954	0.6253	96.0	98.6
9	0.2879	0.2098	0.5023	0.2887	0.1026	0.6087	92.0	98.5
10	0.2344	0.3168	0.4488	0.2999	0.1103	0.5898	80.5	98.4

Table XII.23 Experiment 20

Stage No.	Experimental formaldehyde wt fraction	Experimental methanol wt fraction	Experimental water wt fraction	Calculated formaldehyde wt fraction	Calculated methanol wt fraction	Calculated water wt fraction	T _{exp} (°C)	T _{cal} (°C)
1	0.3998	0.0010	0.5992	0.3958	0.0090	0.5952	100.2	98.9
2	0.3686	0.0026	0.6286	0.3794	0.0097	0.6109	99.6	98.7
3	0.3651	0.0077	0.6272	0.3709	0.0119	0.6172	99.5	98.7
4	0.3587	0.0140	0.6272	0.3660	0.0142	0.6198	99.0	101.6
5	0.3551	0.0267	0.6182	0.2939	0.0677	0.6385	98.7	99.7
6	0.3356	0.0339	0.6305	0.2631	0.0785	0.6583	98.5	98.9
7	0.3293	0.0410	0.6297	0.2692	0.0905	0.6403	98.2	98.6
8	0.3126	0.0867	0.6007	0.2768	0.1001	0.6231	96.5	98.4
9	0.2934	0.1552	0.5514	0.2885	0.1079	0.6036	94.0	98.3
10	0.2394	0.2914	0.4693	0.2996	0.1158	0.5846	81.0	98.3

Table XII.24 Experiment 21

Stage No.	Experimental formaldehyde wt fraction	Experimental methanol wt fraction	Experimental water wt fraction	Calculated formaldehyde wt fraction	Calculated methanol wt fraction	Calculated water wt fraction	T _{exp} (°C)	T _{cal} (°C)
1	0.3971	0.0038	0.5991	0.3971	0.0038	0.5991	99.5	98.9
2	0.3622	0.0076	0.6302	0.3899	0.0039	0.6062	99.0	98.9
3	0.3511	0.0075	0.6414	0.3755	0.0047	0.6198	98.9	98.8
4	0.3349	0.0127	0.6525	0.3632	0.0062	0.6306	98.8	98.7
5	0.3357	0.0175	0.6469	0.3536	0.0088	0.6376	98.8	98.6
6	0.3275	0.0534	0.6191	0.3445	0.0134	0.6421	97.8	98.5
7	0.3114	0.0682	0.6024	0.3349	0.0215	0.6436	97.0	101.3
8	0.3056	0.1401	0.5543	0.2716	0.0935	0.6349	94.2	98.6
9	0.2861	0.2098	0.5041	0.1397	0.2385	0.6218	89.5	87.8
10	0.1607	0.4400	0.3993	0.0867	0.4355	0.4779	76.3	80.5

Table XII.25 Experiment 22

Stage No.	Experimental formaldehyde wt fraction	Experimental methanol wt fraction	Experimental water wt fraction	Calculated formaldehyde wt fraction	Calculated methanol wt fraction	Calculated water wt fraction	T _{exp} (°C)	T _{cal} (°C)
1	0.3906	0.0010	0.6084	0.3861	0.0100	0.6039	99.2	98.8
2	0.3625	0.0075	0.6300	0.3707	0.0113	0.6180	98.9	98.7
3	0.3620	0.0075	0.6305	0.3616	0.0145	0.6239	98.7	101.6
4	0.3543	0.0286	0.6171	0.2835	0.0728	0.6436	98.2	99.4
5	0.3415	0.0264	0.6321	0.2545	0.0830	0.6624	97.8	98.7
6	0.3247	0.0455	0.6297	0.2631	0.0953	0.6416	97.2	98.4
7	0.3265	0.0720	0.6015	0.2720	0.1045	0.6235	97.0	98.2
8	0.3027	0.1291	0.5682	0.2861	0.1123	0.6016	94.8	98.1
9	0.2485	0.2591	0.4924	0.2964	0.1185	0.5851	90.0	98.1
10	0.1972	0.3735	0.4293	0.3094	0.1254	0.5652	78.5	98.2

Table XII.26 Experiment 23

Stage No.	Experimental formaldehyde wt fraction	Experimental methanol wt fraction	Experimental water wt fraction	Calculated formaldehyde wt fraction	Calculated methanol wt fraction	Calculated water wt fraction	T _{exp} (°C)	T _{cal} (°C)
1	0.3952	0.0010	0.6038	0.3907	0.0100	0.5993	99.8	98.8
2	0.3744	0.0039	0.6218	0.3742	0.0111	0.6147	99.0	98.7
3	0.2910	0.0099	0.6992	0.3647	0.0141	0.6211	98.8	101.6
4	0.3551	0.0229	0.6220	0.2848	0.0730	0.6422	98.6	99.4
5	0.3452	0.0203	0.6345	0.2534	0.0931	0.6535	98.2	98.3
6	0.3327	0.0319	0.6354	0.2632	0.1068	0.6300	97.8	97.9
7	0.3220	0.0533	0.6247	0.2737	0.1171	0.6092	97.5	97.8
8	0.3107	0.1016	0.5877	0.2875	0.1258	0.5867	95.8	97.7
9	0.2769	0.2058	0.5172	0.2987	0.1325	0.5688	92.2	97.7
10	0.2229	0.3336	0.4435	0.3121	0.1400	0.5479	79.0	97.8

Table XII.27 Experiment 24

Stage No.	Experimental formaldehyde wt fraction	Experimental methanol wt fraction	Experimental water wt fraction	Calculated formaldehyde wt fraction	Calculated methanol wt fraction	Calculated water wt fraction	T _{exp} (°C)	T _{cal} (°C)
1	0.3938	0.0040	0.6024	0.3908	0.0098	0.5994	99.2	98.8
2	0.3664	0.0063	0.6274	0.3742	0.0109	0.6149	99.1	98.7
3	0.3623	0.0074	0.6303	0.3646	0.0139	0.6216	99.0	101.6
4	0.3574	0.0218	0.6208	0.2847	0.0724	0.6429	98.8	99.4
5	0.3480	0.0187	0.6333	0.2527	0.0953	0.6520	98.7	98.2
6	0.3422	0.0180	0.6398	0.2634	0.1093	0.6273	98.1	97.9
7	0.3268	0.0277	0.6455	0.2755	0.1198	0.6047	98.0	97.7
8	0.3049	0.0620	0.6331	0.2883	0.1286	0.5831	96.7	97.7
9	0.2768	0.1262	0.5970	0.3006	0.1354	0.5639	94.5	97.7
10	0.2585	0.2493	0.4922	0.3146	0.1430	0.5425	85.0	97.7

Table XII.28 Experiment 25

Stage No.	Experimental formaldehyde wt fraction	Experimental methanol wt fraction	Experimental water wt fraction	Calculated formaldehyde wt fraction	Calculated methanol wt fraction	Calculated water wt fraction	T _{exp} (°C)	T _{cal} (°C)
1	0.4041	0.0010	0.5949	0.4037	0.0110	0.5854	99.0	99.0
2	0.3621	0.0075	0.6304	0.3959	0.0076	0.5965	98.7	98.9
3	0.3517	0.0062	0.6421	0.3868	0.0083	0.6049	98.8	98.8
4	0.3465	0.0125	0.6410	0.3786	0.0096	0.6118	98.6	98.7
5	0.3337	0.0137	0.6526	0.3716	0.0115	0.6169	98.4	98.7
6	0.3235	0.0340	0.6425	0.3647	0.0143	0.6210	97.8	101.6
7	0.3236	0.0620	0.6144	0.3362	0.0610	0.6028	97.0	100.3
8	0.3084	0.1197	0.5719	0.2669	0.1355	0.5975	95.0	97.0
9	0.2582	0.2661	0.4756	0.1878	0.2373	0.5749	91.0	88.8
10	0.1626	0.4580	0.3794	0.1431	0.3394	0.5176	76.4	84.4

Table XII.29 Experiment 1

Stage No.	Formaldehyde efficiency	Hemiformal efficiency	Methanol efficiency	Methylene glycol efficiency	Water efficiency	Weir height (mm)
2	0.1277	0.2723	0.1660	0.3386	0.9536	28
3	0.2097	0.2547	0.1299	0.3409	-0.2566	26
4	0.0886	0.2417	0.1169	0.3441	0.1642	40
5	0.1512	0.2275	0.0839	0.3443	-0.0370	31
6	0.1799	0.2708	0.0646	0.3452	-0.0787	29
7	0.1689	0.2654	0.0510	0.3464	-0.0590	31
8	1.2909	1.3226	1.1601	1.6032	1.1548	31
9	1.0027	1.4741	0.9827	1.6015	0.9408	33

Table XII.30 Experiment 2

Stage No.	Formaldehyde efficiency	Hemiformal efficiency	Methanol efficiency	Methylene glycol efficiency	Water efficiency	Weir height (mm)
2	0.1484	0.2786	0.1767	0.3376	2.2152	28
3	0.1778	0.2527	0.1367	0.3396	-0.0527	26
4	0.0597	0.2350	0.1191	0.3431	0.2260	40
5	0.1027	0.2150	0.0848	0.3431	0.0369	31
6	0.0156	-0.0494	0.0834	0.3427	0.0845	29
7	-0.0359	0.1887	0.0660	0.3410	0.1331	31
8	0.7208	1.3848	1.1557	1.6005	1.4251	31
9	0.9674	1.4624	0.9746	1.6017	0.9175	33

Table XII.31 Experiment 3

Stage No.	Formaldehyde efficiency	Hemiformal efficiency	Methanol efficiency	Methylene glycol efficiency	Water efficiency	Weir height (mm)
2	-0.1921	0.3477	0.2781	0.3324	-1.1934	28
3	0.0324	0.3110	0.2305	0.3330	-0.3634	26
4	0.0234	0.2799	0.2043	0.3395	-0.4273	40
5	0.1249	0.2602	0.1666	0.3394	0.0036	31
6	0.1413	0.2471	0.1401	0.3393	0.1845	29
7	0.1306	0.2355	0.1190	0.3411	-0.7049	31
8	1.8652	1.6013	1.1504	1.6008	-2.7456	31
9	1.2725	1.6075	0.9496	1.6003	0.9371	33

Table XII.32 Experiment 4

Stage No.	Formaldehyde efficiency	Hemiformal efficiency	Methanol efficiency	Methylene glycol efficiency	Water efficiency	Weir height (mm)
2	0.0455	0.3060	0.2227	0.3349	-0.6557	28
3	0.1799	0.2841	0.1811	0.3385	0.1597	26
4	0.0535	0.2659	0.1643	0.3413	-3.915	40
5	0.1241	0.2485	0.1298	0.3415	0.1907	31
6	0.1540	0.2387	0.1076	0.3420	-0.2170	29
7	0.1416	0.2289	0.0912	0.3435	-0.0810	31
8	1.7124	1.5616	1.1426	1.6008	0.0669	31
9	1.2200	1.5745	0.9468	1.6004	0.9242	33

Table XII.33 Experiment 5

Stage No.	Formaldehyde efficiency	Hemiformal efficiency	Methanol efficiency	Methylene glycol efficiency	Water efficiency	Weir height (mm)
2	0.0422	0.7404	0.6683	0.5932	-0.2884	28
3	0.2600	0.5561	0.4428	0.5393	-0.0230	26
4	0.2214	0.4907	0.3738	0.5422	-0.6622	40
5	0.2812	0.4581	0.3035	0.5437	0.4817	31
6	0.3006	0.4316	0.2469	0.5460	0.1289	29
7	0.2765	0.4289	0.2019	0.5481	0.1115	31
8	1.1121	0.9068	0.9364	1.4013	0.8821	31
9	0.6870	1.1416	0.7831	1.4014	0.7721	33

Table XII.34 Experiment 6

Stage No.	Formaldehyde efficiency	Heniformal efficiency	Methanol efficiency	Methylene glycol efficiency	Water efficiency	Weir height (mm)
2	0.2554	0.7468	0.6657	0.6237	0.8111	28
3	0.1121	0.7382	0.6395	0.8592	-0.3107	26
4	0.2224	0.5924	0.4773	0.6416	-2.4168	40
5	0.2822	0.5232	0.3628	0.6438	0.5651	31
6	0.4030	0.4349	0.2894	0.6429	0.2407	29
7	0.0332	0.4148	0.2359	0.6461	0.3008	31
8	-0.0583	0.3937	0.1961	0.6491	0.2430	31
9	-0.0549	0.3680	0.1651	0.6497	0.1783	33

Table XII.35 Experiment 7

Stage No.	Formaldehyde efficiency	Hemiformal efficiency	Methanol efficiency	Methylene glycol efficiency	Water efficiency	Weir height (mm)
2	0.1684	0.2379	0.1101	0.3418	-0.0573	28
3	0.2009	0.2321	0.0847	0.3434	-0.1196	26
4	0.1031	0.2462	0.0785	0.3461	0.0360	40
5	0.1559	0.2430	0.0519	0.3463	-0.0562	31
6	0.1902	0.2685	0.0387	0.3470	-0.0799	29
7	-0.0359	0.1382	0.0425	0.3495	0.0747	31
8	0.6069	1.4022	1.1527	1.6003	1.2795	31
9	0.9584	1.4786	0.9699	1.6017	0.9189	33

Table XII.36 Experiment 8

Stage No.	Formaldehyde efficiency	Hemiformal efficiency	Methanol efficiency	Methylene glycol efficiency	Water efficiency	Weir height (mm)
2	0.5925	1.1062	1.0318	0.9714	0.9436	28
3	0.3449	1.1098	1.0297	0.9714	1.3808	26
4	0.3798	1.0623	1.0123	0.9818	2.5525	40
5	0.5032	1.0738	1.0061	0.9787	8.6547	31
6	0.4840	1.0986	0.9825	1.0481	0.2468	29
7	0.7457	0.9686	0.7748	0.9957	0.4723	31
8	0.7347	0.9175	0.6365	0.9998	0.5400	31
9	0.6568	0.7354	0.4994	1.0002	0.4730	33

Table XII.37 Experiment 9

Stage No.	Formaldehyde efficiency	Hemiformal efficiency	Methanol efficiency	Methylene glycol efficiency	Water efficiency	Weir height (mm)
2	-0.0215	0.4423	0.3704	0.3254	1.0362	28
3	-0.4970	0.4397	0.3658	0.3222	3.5495	26
4	-0.1854	0.4643	0.4324	0.3624	-0.4855	40
5	-0.0141	0.3693	0.2995	0.3310	-0.2923	31
6	-0.1514	0.3182	0.2536	0.3377	-0.6372	29
7	-0.0352	0.2809	0.2170	0.3314	-0.3294	31
8	0.2140	0.8629	0.7574	0.9908	-0.4626	31
9	0.7240	0.8079	0.6745	0.9918	0.4672	33

Table XII.38 Experiment 10

Stage No.	Formaldehyde efficiency	Hemiformal efficiency	Methanol efficiency	Methylene glycol efficiency	Water efficiency	Weir height (mm)
2	0.4718	0.6383	0.4934	0.6420	0.1907	28
3	0.5175	0.5761	0.3654	0.6473	0.1513	26
4	0.4817	0.4425	0.2940	0.6481	0.2491	40
5	0.1037	0.4606	0.2191	0.6499	0.2347	31
6	0.0352	0.4438	0.1737	0.6509	0.1723	29
7	0.0593	0.2641	0.1425	0.6505	0.1356	31
8	0.0634	-0.0331	0.1151	0.6504	0.1284	30
9	-0.0699	0.3343	0.1043	0.6508	0.0849	36

Table XII.39 Experiment 11

Stage No.	Formaldehyde efficiency	Hemiformal efficiency	Methanol efficiency	Methylene glycol efficiency	Water efficiency	Weir height (mm)
2	0.5560	1.1161	1.0332	0.9712	0.8185	28
3	0.6472	1.1116	1.0323	0.9704	1.0411	26
4	0.1705	1.0650	1.0161	0.9785	1.8254	40
5	0.4021	1.0787	1.0133	0.9784	4.4795	31
6	0.5442	1.0738	1.0020	0.9761	-17.1493	29
7	0.9213	1.5199	1.3576	1.4910	0.6782	31
8	1.3072	1.4210	1.0457	1.4508	0.5969	30
9	1.0330	1.3781	0.8515	1.4505	0.8407	36

Table XII.40 Experiment 12

Stage No.	Formaldehyde efficiency	Hemiformal efficiency	Methanol efficiency	Methylene glycol efficiency	Water efficiency	Weir height (mm)
2	0.1703	0.2459	0.1488	0.3372	0.4964	28
3	0.1723	0.2301	0.1195	0.3388	-0.4804	26
4	0.0717	0.2219	0.1096	0.3427	0.2138	40
5	0.1314	0.2071	0.0792	0.3427	-0.0820	31
6	0.1544	0.2546	0.0628	0.3434	-0.1188	29
7	1.1147	1.1894	1.0727	1.4520	1.0818	31
8	0.9211	1.2676	0.8896	1.4515	0.8563	30
9	0.7211	0.9189	0.7674	1.4506	0.7457	36

Table XII.41 Experiment 13

Stage No.	Formaldehyde efficiency	Hemiformal efficiency	Methanol efficiency	Methylene glycol efficiency	Water efficiency	Weir height (mm)
2	0.5396	1.1108	1.0339	0.9671	0.9860	28
3	0.0786	1.1088	1.0329	0.9676	1.8019	26
4	0.2426	1.0730	1.0191	0.9744	4.7769	40
5	0.3922	1.0692	1.0110	0.9810	-13.1231	31
6	0.3938	1.0713	0.9708	1.0431	0.1290	29
7	1.1666	1.3993	1.1555	1.4482	1.1270	31
8	1.1229	1.2393	0.9389	1.4502	0.9184	30
9	0.6423	1.1975	0.7991	1.4513	0.7896	36

Table XII.42 Experiment 14

Stage No.	Formaldehyde efficiency	Hemiformal efficiency	Methanol efficiency	Methylene glycol efficiency	Water efficiency	Weir height (mm)
2	0.9663	0.9176	0.7043	0.9969	3.0163	28
3	0.8526	0.3579	0.5622	0.9993	0.4009	26
4	0.3823	0.1412	0.4700	1.0007	0.4866	40
5	0.2785	0.5456	0.3849	1.0008	0.3720	31
6	0.3226	0.6226	0.3282	1.0003	0.2937	27
7	0.3531	0.8115	0.2971	1.0001	0.2529	32
8	0.3632	0.8941	0.2666	1.0001	0.2397	30
9	0.3754	0.9407	0.2518	1.0000	0.2403	36

Table XII.43 Experiment 15

Stage No.	Formaldehyde efficiency	Hemiformal efficiency	Methanol efficiency	Methylene glycol efficiency	Water efficiency	Weir height (mm)
2	0.1177	0.3086	0.2373	0.3329	-0.1444	28
3	0.1506	0.2848	0.1960	0.3350	0.0027	26
4	0.0404	0.2637	0.1764	0.3396	-0.7712	40
5	0.1214	0.2444	0.1408	0.3398	-0.0268	31
6	1.3934	1.2289	0.9140	1.3004	-26.4285	27
7	1.0531	1.1951	0.7523	1.3004	0.7115	32
8	0.5521	0.5733	0.6396	1.3009	0.6460	30
9	0.5561	0.7910	0.5765	1.3002	0.5578	36

Table XII.44 Experiment 16

Stage No.	Formaldehyde efficiency	Hemiformal efficiency	Methanol efficiency	Methylene glycol efficiency	Water efficiency	Weir height (mm)
2	0.0443	0.1916	0.1041	0.2355	0.3424	28
3	0.0762	0.1795	0.0847	0.2367	-0.0057	26
4	-0.0554	0.1698	0.0836	0.2398	-2.1041	40
5	0.0168	0.1565	0.0615	0.2379	-0.3551	31
6	0.8754	0.8020	0.5987	0.8976	3.7416	27
7	0.7196	0.6796	0.4948	0.8983	0.4093	32
8	0.3239	0.6646	0.3993	0.9010	0.4008	30
9	0.2539	0.4763	0.3394	0.9007	0.3296	36

Table XII.45 Experiment 17

Stage No.	Formaldehyde efficiency	Hemiformal efficiency	Methanol efficiency	Methylene glycol efficiency	Water efficiency	Weir height (mm)
2	0.0049	0.7370	0.4824	0.4158	-0.0376	28
3	0.1043	0.5023	0.4643	0.4185	0.0836	26
4	0.0302	0.4905	0.4597	0.4226	0.0067	40
5	0.1010	0.6434	0.7129	0.5054	-0.2123	31
6	0.6610	0.7655	0.6467	0.7896	0.6637	27
7	0.6145	0.7213	0.5397	0.7953	1.1960	32
8	0.5927	0.6937	0.4160	0.7997	0.2219	30
9	0.6358	0.5281	0.3328	0.7999	0.2736	36

Table XII.46 Experiment 18

Stage No.	Formaldehyde efficiency	Hemiformal efficiency	Methanol efficiency	Methylene glycol efficiency	Water efficiency	Weir height (mm)
2	1.0794	1.3500	1.5461	1.4662	1.0254	28
3	1.1328	1.5898	1.5173	1.4662	0.9618	26
4	0.9108	1.5378	1.4061	1.5012	0.5837	41
5	-0.0797	0.1960	0.0864	0.2385	0.8632	34
6	-0.0782	0.1676	0.0796	0.2367	2.1382	31
7	-0.0814	0.1553	0.0557	0.2362	1.2631	32
8	-0.1439	0.1389	0.0467	0.2342	1.7327	30
9	-0.1061	0.1334	0.0477	0.2368	3.3043	39

Table XII.47 Experiment 19

Stage No.	Formaldehyde efficiency	Hemiformal efficiency	Methanol efficiency	Methylene glycol efficiency	Water efficiency	Weir height (mm)
2	1.0889	1.2114	1.5455	1.4663	1.0443	28
3	1.1344	1.5911	1.5191	1.4662	0.9641	26
4	0.9484	1.5498	1.4238	1.5033	0.6559	41
5	-0.0647	0.2047	0.0932	0.2390	0.9284	34
6	-0.0625	0.1754	0.0929	0.2375	31.3533	31
7	-0.1233	0.1635	0.0627	0.2369	3.1112	32
8	-0.0937	0.1503	0.0495	0.2353	4.1172	30
9	-0.0108	0.1427	0.0535	0.2375	13.0443	39

Table XII.48 Experiment 20

Stage No.	Formaldehyde efficiency	Hemiformal efficiency	Methanol efficiency	Methylene glycol efficiency	Water efficiency	Weir height (mm)
2	1.0835	1.8517	1.5517	1.4661	1.0099	28
3	1.1315	1.5871	1.5188	1.4659	0.9916	26
4	0.9468	1.5475	1.4292	1.5030	0.6544	41
5	-0.0664	0.2049	0.0942	0.2388	1.0176	34
6	-0.0701	0.1611	0.0840	0.2370	2.7069	31
7	-0.0799	0.1628	0.0619	0.2366	1.4999	32
8	-0.1125	0.1473	0.0509	0.2350	1.6557	30
9	-0.1050	0.1403	0.0520	0.2372	2.5372	39

Table XII.49 Experiment 21

Stage No.	Formaldehyde efficiency	Hemiformal efficiency	Methanol efficiency	Methylene glycol efficiency	Water efficiency	Weir height (mm)
2	0.7239	1.6306	1.2106	1.1145	0.7207	28
3	0.7751	1.2960	1.1873	1.1146	0.7562	26
4	0.7308	1.2129	1.1638	1.1238	0.6746	41
5	0.7606	1.2179	1.1675	1.1215	0.6326	34
6	0.7859	1.2141	1.1567	1.1215	0.5090	31
7	0.5406	1.1907	1.0573	1.1467	0.0863	32
8	1.0022	1.0726	0.8020	1.1494	-0.2110	30
9	0.8354	0.7520	0.6512	1.1502	0.6069	39

Table XII.50 Experiment 22

Stage No.	Formaldehyde efficiency	Hemiformal efficiency	Methanol efficiency	Methylene glycol efficiency	Water efficiency	Weir height (mm)
2	1.1065	1.7035	1.5306	1.4669	1.0032	28
3	0.9667	1.6536	1.4633	1.4992	0.6592	26
4	-0.0842	0.1992	0.0894	0.2393	0.8716	36
5	-0.0877	0.1697	0.0792	0.2375	1.7852	33
6	-0.0873	0.1569	0.0559	0.2359	1.1881	31
7	-0.1269	0.1424	0.0489	0.2351	1.5124	32
8	-0.0921	0.1311	0.0380	0.2341	1.9209	30
9	-0.1115	0.1260	0.0452	0.2364	5.0540	39

Table XII.51 Experiment 23

Stage No.	Formaldehyde efficiency	Heniformal efficiency	Methanol efficiency	Methylene glycol efficiency	Water efficiency	Weir height (mm)
2	1.0976	1.8362	1.5371	1.4669	1.0006	28
3	0.9802	1.6688	1.4744	1.4988	0.6779	26
4	-0.0771	0.2000	0.0905	0.2394	0.8454	36
5	-0.0936	0.1679	0.0750	0.2371	0.8237	33
6	-0.0960	0.1510	0.0547	0.2353	0.6671	31
7	-0.1189	0.1363	0.0468	0.2347	0.7741	32
8	-0.0951	0.1241	0.0364	0.2336	0.7799	30
9	-0.1104	0.1194	0.0428	0.2361	1.2186	39

Table XII.52 Experiment 24

Stage No.	Formaldehyde efficiency	Heniformal efficiency	Methanol efficiency	Methylene glycol efficiency	Water efficiency	Weir height (mm)
2	1.1068	1.1825	1.5378	1.4468	1.0149	28
3	0.9723	1.6698	1.4771	1.4984	0.6715	26
4	-0.0793	0.2009	0.0924	0.2393	0.8976	36
5	-0.0999	0.1667	0.0757	0.2368	0.7911	33
6	-0.1089	0.1487	0.0556	0.2348	0.6938	31
7	-0.1109	0.1345	0.0469	0.2343	0.7450	32
8	-0.1030	0.1211	0.0376	0.2331	0.8259	30
9	-0.1132	0.1166	0.0431	0.2357	1.3038	39

Table XII.53 Experiment 25

Stage No.	Formaldehyde efficiency	Hemiformal efficiency	Methanol efficiency	Methylene glycol efficiency	Water efficiency	Weir height (mm)
2	0.3790	0.8117	0.8411	0.7612	0.3751	28
3	0.3832	0.9803	0.8402	0.7606	0.3664	26
4	0.3581	0.8789	0.8215	0.7676	0.3227	36
5	0.3706	0.8717	0.8183	0.7667	0.3073	33
6	0.2183	0.9314	0.8602	0.7604	-0.1229	31
7	0.4955	0.7201	0.5931	0.7897	0.1879	32
8	0.5199	0.6573	0.4586	0.7961	0.2964	30
9	0.5395	0.4335	0.3782	0.7981	0.3062	39

APPENDIX XIII CORRECTION FOR LOW METHANOL CONTENT

The program BUBLDILF was applied to a wide range of concentration, and very good agreement was obtained between the calculated and experimental results, except for the region of 0.01 to 0.12 mole fraction of methanol in the liquid phase. The reason for the error have been discussed earlier. However, in order to proceed with the distillation calculations, results for this region of concentration were essential. Therefore correction of the calculated vapour phase mole fractions was attempted.

The difference between the calculated and experimental vapour phase mole fractions was calculated and a polynomial was fitted to the difference as a function of liquid phase mole fractions, using optimisation techniques. In order to reduce the number of variables, the quinary system was reduced to the original ternary system of formaldehyde-methanol-water. The correction is applied at the end of the calculations and therefore the phase and chemical equilibria calculations are not affected by the correction. The correction is only applied to the region of 0.01 to 0.12 mole fraction of methanol in the liquid phase.

The correlation for each component is in term of equation XIII.1.

$$\Delta Y = A X01^B + C X03^D + E X05^F + G \quad \text{(XIII.1)}$$

where

$$\Delta Y = Y_{\text{exp}} - Y_{\text{cal}} \quad (\text{XIII.2})$$

and constants A to G are the parameters of the polynomial. X01, X03 and X05 are the liquid phase mole fraction of the ternary system of formaldehyde, methanol and water.

The values of ΔY were calculated at several points. Marquardt's (225) method was used to estimate the parameters A to G.

Some of the calculated and experimental values (41,67) are represented in Table XIII.1, where F, M and W represent formaldehyde, methanol and water respectively.

The correction equations are given for three components in equations XIII.3 to XIII.5

$$Y_{01\text{cor}} = Y_{01\text{cal}} - 0.1449 X_F^{0.3414} + 0.9435 X_M^{1.5080} + 0.0166 \quad (\text{XIII.3})$$

$$Y_{03\text{cor}} = Y_{03\text{cal}} + 0.5142 X_F^{0.7975} + 0.9052 X_M^{0.0340} + 0.1859 X_W^{5.0} - 0.9533 \quad (\text{XIII.4})$$

$$Y_{05\text{cor}} = Y_{05\text{cal}} + 0.2224 X_F^{0.1763} + 0.8390 X_M^{-0.0212} + 0.0982 X_W^{2.2858} - 1.1019 \quad (\text{XIII.5})$$

Table XIII.1

Component	X _{exp} mole fraction	Y _{exp} mole fraction	Y _{cal} mole fraction	ΔY mole fraction	T _{exp} K	T _{cal} K	ΔT K
F	0.1549	0.1343	0.1835	-0.0492	369.9	367.3	2.6
M	0.0435	0.1219	0.0815	0.0404			
W	0.8016	0.7438	0.7349	0.0089			
F	0.2043	0.1636	0.2300	-0.0664	370.5	367.4	3.1
M	0.0333	0.0916	0.0443	0.0473			
W	0.7624	0.7448	0.7256	0.0192			
F	0.2535	0.1989	0.2731	-0.0742	371.3	367.3	4.0
M	0.0146	0.0447	0.0132	0.0315			
W	0.7318	0.7564	0.7137	0.0427			
F	0.2662	0.1902	0.2519	-0.0617	369.7	367.0	2.7
M	0.0621	0.1374	0.0605	0.0769			
W	0.6716	0.6724	0.6874	-0.015			
F	0.3169	0.2312	0.3044	-0.0732	371.5	367.2	4.3
M	0.0110	0.0455	0.0063	0.0392			
W	0.6721	0.7232	0.6894	0.0338			
F	0.3026	0.2084	0.2744	-0.066	370.1	367.4	2.7
M	0.0560	0.1252	0.0437	0.0815			
W	0.6413	0.6664	0.6819	-0.0155			
F	0.0144	0.0164	0.0209	-0.0045	366.9	366.9	0.0
M	0.0422	0.2271	0.2124	0.0147			
W	0.9434	0.7565	0.7667	-0.0102			
F	0.0314	0.0341	0.0574	-0.0233	372.1	371.0	1.1
M	0.0081	0.0379	0.0433	-0.0054			
W	0.9605	0.9280	0.8992	0.0288			

Table XIII.1 continued

Component	X _{exp} mole fraction	Y _{exp} mole fraction	Y _{cal} mole fraction	ΔY mole fraction	T _{exp} K	T _{cal} K	ΔT K
F	0.0649	0.0649	0.0997	-0.0348	370.8	369.0	1.8
M	0.0221	0.0789	0.0825	-0.0036			
W	0.9130	0.8561	0.8178	0.0383			
F	0.0994	0.0932	0.1430	-0.0498	370.7	368.7	2.0
M	0.0212	0.0810	0.0605	0.0205			
W	0.8793	0.8258	0.7964	0.0294			

It was found that the average ΔT is equal to three degrees centigrade where the correction is represented by equation XIII.6

$$T_{\text{cor}} = T_{\text{cal}} + 3.0 \quad (\text{XIII.6})$$

APPENDIX XIV ESTIMATED PARAMETERS

The program COMP5 was unable to estimate the Henry's constants due to the reasons which have been discussed earlier.

The value of Henry's constant does not affect the phase and chemical equilibria calculations because of the very large positive, Wilson's single energy parameter and very low formaldehyde concentration in the liquid. The generalised estimation techniques are also inadequate, since there are no binary data available for formaldehyde with any other component in the system. However although the values of Henry's constant are redundant in the calculations an approximate value could be obtained assuming an ideal solution and vapour phase. The components in the solution are assumed to be a single component. These assumptions could be used for estimation of order of magnitude of the Henry's constant.

The Henry's law for the ideal vapour and liquid phases are represented by equation XIV.1

$$H = \frac{p}{X} \qquad \text{(XIV.1)}$$

where p and X are the partial pressure and liquid mole fraction of formaldehyde.

The values of H at three different temperatures are

listed in Table XIV.1

Table XIV.1

T (K)	H (kNm ⁻²)
340.1	810.60
359.1	2618.24
370.6	3924.32

The estimated parameters from program COMP5 are listed in Table XIV.2. The components, formaldehyde to water are numbered from 1 to 5 respectively. The values of energy parameters are denoted by λ .

Table XIV.2

Binary system i-j	Wilson's energy parameter $\lambda_{ij} - \lambda_{ii}$ (kJ/mol)	Wilson's energy parameter $\lambda_{ij} - \lambda_{jj}$ (kJ/mol)
2-3	- 97.450	316.291
2-4	185.509	418.181
2-5	4.167	4181.814
3-4	- 0.245	- 1.945
3-5	1.636	1.360
4-5	- 3.110	1062.937

The Wilson's single parameter for formaldehyde in the reference component, water is estimated at 465.672 kJ/mol.

The energy parameters will have to be converted to cal/mol in order to be used directly in the computer programs. The conversion factor is that one Kilo-Joules is equivalent to 238.892 calories.